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LVIII. *On the L-absorption Spectra of the Elements from Sn (50) to W (74) and their Relation to the Atomic Constitution.* By Y. NISHINA, *Physicist, the Institute of Physical and Chemical Research, Tokio* *.

[Plate VIII.]

Introduction and Summary of Results.

BOHR and Coster emphasized † the characteristic features displayed by Moseley's curves in those parts of the natural system where, according to Bohr's theory, the completion of inner groups of electrons in the atoms is in progress, *i. e.* in the neighbourhood of iron-, palladium-, and platinum-groups as well as the rare earths. In a paper by Coster, Werner, and the present writer ‡, the result of the measurements of the L-absorption spectra of nine elements between La (57) and Hf (72) was given. These measurements agreed well with the interpolated values which were used by Bohr and Coster in their paper. In view of the importance of more accurate values of the energy levels free from the uncertainty involved in the interpolation and arising from the lack of uniformity of the measurements of different authors, the present writer has undertaken the further measurements of X-ray absorption spectra in general. This

* Communicated by Prof. N. Bohr.

† *Zs. für Phys.* xii. p. 342 (1923).

‡ *Zs. für Phys.* xviii. p. 207 (1923).

paper gives a part of the result of measurements which are still in progress, and it forms the continuation of the work mentioned above*. The results of these measurements enable us to give more exact values of the different energy levels for the elements from Sn (50) to W (74).

A plotting of the square roots of the level values as a function of the atomic number confirms in a striking way the general conclusions of Bohr and Coster. Especially do these curves allow us to trace with considerable certainty the beginning and the end of the gradual development of the group-structure of the atom which takes place within the family of the rare earths. The closer discussion brings some further problems to light, for which, however, neither the theory nor the experiment at present allows of definite conclusions.

Experimental Arrangement and Results.

The apparatus used and its arrangement are the same as mentioned in our previous work†. The vacuum spectrograph and metal X-ray tube of Prof. Siegbahn provided with a mercury vapour pump constitute the main parts. The radius of this spectrograph is 121.4 mm. The source of energy is a transformer of 30,000 volts with a kenotron rectifier (hot cathode rectifier).

The absorption screen is prepared by rubbing the finely-powdered chemical compounds of the elements under examination on a thin sheet of silk paper. As mentioned by Fricke‡, Lindh§, and also by us in the previous work||, the thickness of the material on the screen plays an essential part in obtaining the detailed structure of the absorption spectra. With the thickness of the screen varying from 1 mg. to 7 mg. per sq. cm. of each element, good results were obtained. In order to get good L_I -absorption spectra, which are extremely weak and diffuse in comparison with the L_{III} and L_{II} , a thicker screen is to be used. The screen was placed between the slit and the crystal.

The samples of the rare earths used in the experiment were all presented to this Institute by Freiherr Auer von Welsbach, whose kindness enabled this work to be completed.

* Coster, Nishina, and Werner, *loc. cit.*

† *Loc. cit.*

‡ Phys. Rev. xvi. p. 202 (1920).

§ Dissertation Lund (1923).

|| *Loc. cit.*

The elements which were investigated were in the form of the following compounds:—

74 WO_3 , 73 Ta_2O_5 , 72 HfO_2 , 67 $\text{H}_2\text{O}_2(\text{SO}_4)_3 + \text{aq.}$, 65 Tb_2O_3 ,
64 $\text{Gd}_2(\text{SO}_4)_3 + \text{aq.}$, 63 $\text{Eu}_2(\text{SO}_4)_3 + \text{aq.}$, 62 $\text{Sm}_2(\text{SO}_4)_2 + \text{aq.}$,
60 $\text{Nd}_2(\text{SO}_4)_3 + \text{aq.}$, 59 $\text{Pr}_2(\text{SO}_4)_3 + \text{aq.}$, 56 BaSO_4 ,
55 CsCl , 50 SnO_2 .

In order to get strong continuous radiation a tungsten anticathode was used. After the exposure for absorption spectra, the duration of which ranged from 2 to 15 hours, the exposure for emission lines of reference was generally necessary. For this purpose the tungsten anticathode is replaced by a copper one having the necessary compound on it, which is then exposed for $\frac{1}{4}$ to $\frac{1}{2}$ hour. In case of TaL_I , YbL_{II} , TbL_I , and GdL_I the emission lines $\text{L}\gamma_3$, $\text{L}\beta_2$, $\text{L}\eta$, and $\text{L}\alpha_1$ respectively of tungsten come quite near the absorption edges in question, thus excluding the use of a tungsten anticathode. Generally the hot cathode of the X-ray tube is also of tungsten wire, and in that case some tungsten lines due to a deposit of tungsten on the anticathode cannot be avoided. In order to get rid of these difficulties, tantalum or molybdenum wire, both of which were put at our disposal by the kindness of Prof. Pirani, Studien-Gesellschaft für elektrische Beleuchtung in Berlin, was used for the hot cathode, and the following metals were used as the anticathode:—

For TaL_I , Pt.

For TbL_I , Au.

„ YbL_{II} , Au.

„ GdL_I , Pt.

The tantalum and molybdenum wires, however, burn out in a much shorter time than the tungsten wire, thus making the experiment more troublesome.

The voltage used was never more than twice the critical tension for the absorption spectrum in question. This limitation of voltage prevents the second-order continuous spectrum which is not absorbed by the screen from overlapping and masking the absorption spectrum under examination. The current through the X-ray tube ranged from 8 to 20 milliamperes, according to the metal of the anticathode used. Too much current should be avoided as it results in making a deep hole in the anticathode when the focussing is sharp, and the radiation in the direction of the slit is thereby stopped.

During the exposure the crystal was turned automatically and uniformly to and fro through about one degree in order to get homogeneous exposure on both sides of the absorption edge. Calcite was used as the crystal for all elements except tungsten, for which rock-salt was used.

The method of measurement of the plate is the same as in our previous work*. As will be explained later, the absorption edge appears on the plate as a white line. The distance between the middle of this white line and the middle of the reference emission line is measured by means of Hilger's micrometer. Usually one or two emission lines, each on both sides of the absorption line, are used for reference, and the mean value of the glancing angle obtained from these measurements is used for the calculation of wave-length and frequency.

The results of the measurements are given in Tables I., II., and III. The accuracy of the measurements is about the same as that of our previous work. Usually the error of the measurements of the distance between the absorption line and the reference emission line on the plate is smaller than 0.03 mm. which corresponds to less than 0.7 X.U. in the wave-length. This makes an error in the frequency of 0.1 unit in the case of SnL_{III} and about 0.7 unit in the case of WL_{I} . The error in the L_{III} edge is usually less than this, and in the case of the edges whose figures are given up to the second decimal in the frequency in Table III., the error is less than half the value mentioned.

TABLE I.— L_{I} .

Element.	Glancing angle.	λ .	ν/R .	ν/R interpolated or measured before.
74 W	10° 26.8' (rock-salt)	1020.5	893.0	890.6
73 Ta	10 2.9 (calcite)	1057	862	860.3
72 Hf	10 25.0 "	1095.3	832.0	—
67 Ho	12 32.0 "	1314.6	693.2	692.9
65 Tb	13 32.3 "	1418.1	642.6	642.4
64 Gd	14 4.9 "	1474.0	618.2	617.4
63 Eu	14 39.6 "	1533.3	594.3	593.6
62 Sm	15 16.2 "	1595.4	571.2	570.7
60 Nd	16 36.6 "	1731.7	526.2	525.8
59 Pr	17 21.3 "	1807.1	504.3	504.2
56 Ba	19 54.0 "	2062.0	441.9	442.3
50 Sn	27 10.4 "	2766.7	329.4	—

* *Loc. cit.*

TABLE II.— L_{II} .

Element.	Glancing angle.	λ .	ν/R .	ν/R interpolated or measured before.
74 W	10° 58'4 (rock-salt)	1071.3	850.6	850.1
73 Ta	10 33.6 (calcite)	1110.2	820.8	821.0
70 Yb	11 48.2 „	1239.2	735.4	735.7
67 Ho	13 14.0 „	1386.9	657.1	657.4
65 Tb	14 19.0 „	1498.1	608.3	608.2
63 Eu	15 32.3 „	1622.8	561.5	561.3
62 Sm	16 12.6 „	1699.1	538.9	539.0
60 Nd	17 40.3 „	1839.1	495.5	495.9
59 Pr	18 28.7 „	1920.1	474.6	474.7
56 Ba	21 17.2 „	2199.3	414.3	414.7
55 Cs	22 23.4 „	2307.5	394.9	395.0

TABLE III.— L_{III} .

Element.	Glancing angle.	λ .	ν/R .	ν/R interpolated or measured before.
74 W	12° 25'9 (rock-salt)	1211.6	752.1	751.6
73 Ta	11 55.4 (calcite)	1251.7	728.0	728.6
67 Ho	14 39.0 „	1532.2	594.7	595.0
65 Tb	15 45.5 „	1645.3	553.9	553.8
63 Eu	17 0.3 „	1771.7	514.4	514.1
62 Sm	17 41.4 „	1840.8	495.0	495.0
60 Nd	19 11.0 „	1990.7	457.76	457.9
59 Pr	20 0.5 „	2072.8	439.63	439.4
56 Ba	22 53.6 „	2356.8	386.66	386.7
55 Cs	24 2.1 „	2467.4	369.32	369.5
50 Sn	31 18.0 „	3147.3	289.54	—

Of course, all the errors in the determination of the grating constant of the crystal and the measurements of the wave-length of reference lines come in our results, but we expect these to be very small compared with the error mentioned above.

In the last column of the tables the values given by Bohr and Coster in the above-mentioned work are quoted. Except in the case of L_I , the discrepancies with the measured values lie within the limit of the experimental error in most elements. In case of L_{II} , on the other hand, there exists the same kind of systematic difference of less than 1 unit in frequency in the direction of higher values as was found in our previous measurements, except for W and La, where the difference is very large. In case of TaL_I there exists some doubt as to the identification of the absorption line, because we should expect $PtL_{\beta_{10}}$ quite near the absorption

line in question, and, in fact, the absorption line on the plate seemed sharper on the longer wave-length edge than is usually the case with the L_I -lines. Thus it may be possible that the longer wave-length side of the absorption line is overlapped by $PtL_{\beta_{10}}$. Consequently we should reserve the conclusion as regards the real existence of the rather large difference between the measured value and the interpolated one as shown in the table.

As is well known now, the structure of the absorption spectra is not simple. If the thickness of the absorbing screen is suitably prepared, the X-ray absorption spectra appear on the photographic plate as white lines instead of absorption edges, as was formerly accepted. In some cases, not only the one white line which is measured and given in the above tables, but a second or even a third white line is observed, one closely following the other on the shorter wave-length side of the main absorption line. The general details of such fine structure displayed on the plates which were obtained with the compounds used in this experiment will be described here. We shall take the case of HoL_{III} , and follow the plate from the longer wave-length side to the shorter one. At first we see very dark ground showing nearly unabsorbed incident continuous radiation. Then comes the first very strong and sharp white line, which has about the same width as that of the slit, *i. e.* about 0.1 mm. in our case. This white line is followed by a dark band of the width of about 0.2 mm., the intensity of darkness being usually less than the darkness on the longer wave-length side of the first white line. After this dark band follows again a white line, which is much weaker, broader, and more diffuse than the first one, its width being about 0.13 mm. After passing this second white line, we meet either with the dark ground or a second dark band, according to different elements. In the former case the continuous darkness extends on the shorter wave-length side all over the rest of the plate, the intensity of darkness being usually less than that on the longer wave-length side of the first white line. In the latter case the second dark band, which is broader than the first one—for example, 0.3 mm. wide in case of HoL_{III} —is followed by a third white line, which is much broader, weaker, and more diffuse than the second one. After this white line there follows continuous darkness all over the rest of the plate as in the former case. Whether the difference of these two cases lies in the nature of the phenomena or in the difference of the thickness of the absorbing screen or of the conditions of the experiment, and whether more than three white lines exist or not, remains

still to be decided. Fig. 1 *a* (Pl. VIII.) is the reproduction of the HoL_{III} spectra and fig. 1 *b* is its photometric curve. They show one example of the latter case. Figs. 2 *a* (Pl. VIII.) and 2 *b*, which are the corresponding reproduction of the SmL_{III} spectra and its photometric curve, show, on the other hand, one example of the former case. It seems to the writer that with a thinner absorbing screen the absorption spectra of the former type is obtained, whereas with a thicker one that of the latter type is obtained.

Fig. 1 *b*.

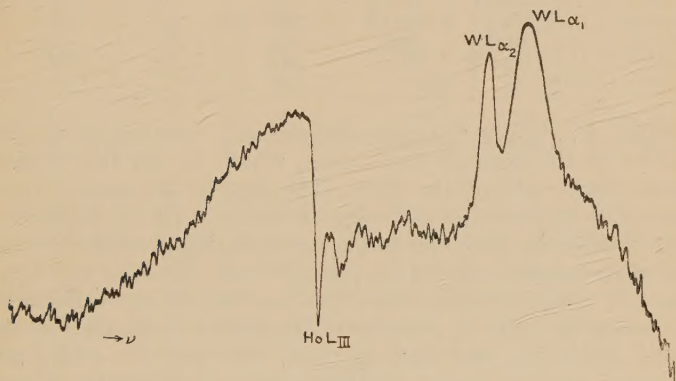
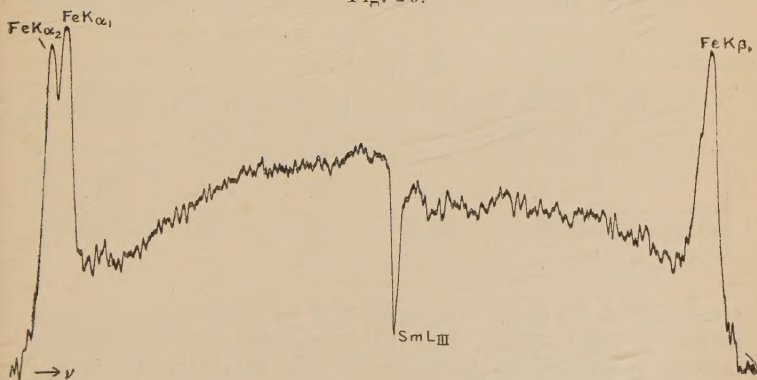


Fig. 2 *b*.



The above description of the fine structure applies generally for the L_{III} -absorption spectra. In the cases of L_{I} and L_{II} such detailed structure is very rarely observed. They show usually only the first white line, especially with L_{I} , no plate

with a second white line having been observed. The first white line in case of L_I , moreover, is very weak, diffuse, and broader than the width of the slit.

TABLE IV.

The second white line lying on the shorter wave-length side of the first L_{III} white line.

	λ .	ν/R .	$\Delta\lambda$.	$\Delta\nu/R$.	ΔV .
67 Ho	1525.7	597.3	6.5	2.6	34
66 Dy	1580.1	576.7	6.9	2.5	34
63 Eu	1763.1	516.9	8.5	2.5	34
62 Sm	1831.7	497.5	9.1	2.5	33
60 Nd	1980.6	460.1	10.1	2.3	32
59 Pr	2061.9	442.0	10.9	2.4	32

Table IV. gives the wave-length and frequency of the middle of the second white lines, which lie on the shorter wave-length side of the first white line in the case of L_{III} -absorption spectra for different elements. In the third and fourth columns of the table the corresponding differences of the wave-length and the frequency from those of the L_{III} -line are given respectively, the corresponding difference expressed in volts by means of Einstein's formula $eV = h\nu$ being added in the last column. As will be seen, $\Delta\lambda$ decreases systematically with the atomic number, the corresponding $\Delta\nu/R$ and ΔV being nearly constant. Here the accuracy of the measurement is not high owing to the

TABLE V.

The third white line lying on the shorter wave-length side of the second L_{III} white line.

	λ .	ν/R .	$\Delta\lambda$.	$\Delta\nu/R$.	ΔV .
67 Ho	1515	601.3	17	6.6	89

weakness of the line. The error will be about twice as large as that of the L_{III} -line. In the case of Ho, the wave-length and the frequency of the middle of the third white line lying on the shorter wave-length side of L_{III} could be roughly measured. Their values and their differences from those of L_{III} are given in Table V. On some other plates we can see the third white lines of the same sort, but they are too weak to be measured.

TABLE VI.

Emission lines.	Glancing angles. Calcite.	λ .	ν/R .	$\sqrt{\nu/R}$.
72 Hf $L\beta_7$	12° 24'9"	1302.5	699.7	26.451
Hf $L\beta_9$	12 16.0	1287.0	708.1	26.609
Hf $L\beta_{5, 10}$	12 20.6	1296.7	703.7	26.527
63 Eu $L\gamma_4$	14 44.0	1540.7	591.5	24.320
58 Ce $L\delta$	28 26.8	2885.7	315.79	17.771
55 Cs $L\delta$	32 33.1	3259.6	279.57	16.720
53 I $L\delta$	35 52.2	3549.7	256.72	16.022
I $L\beta_4$	28 39.8	2905.9	313.60	17.709
I $L\beta_6$	27 51.3	2830.5	321.95	17.943
I $L\beta_3$	28 15.5	2868.2	317.72	17.825
I $L\gamma_{2,3}$	23 46.3	2442.1	373.16	19.317
I $L\gamma_4$	23 11.8	2386.2	381.89	19.542

Table VI. gives the result of the measurements of some emission lines which have not been measured accurately and are necessary for the calculation of the energy values of other levels in the next paragraph. The accuracy of these measurements is about the same as in the case of the absorption edges mentioned above, since most of these emission lines are weak and diffuse.

The Values of the Energy Levels.

According to Coster's scheme, the results of our previous work and the present one enable us to calculate the values of different energy levels of different atoms by means of the frequency values of emission lines. In doing this, the values given by the following experimental results were consulted :—

- L-Absorption ... 74 W-50 Sn, Coster, Nishina, and Werner, *Zs. für Phys.* xviii. p. 207 (1923), and the present measurements.
 53 I-50 Sn, Coster *Zs. für Phys.* xxv. p. 83 (1924).
 56 Ba-51 Sb, Lindsay, *C. R.* clxxv. p. 150 (1922).
- L-Emission lines 74 W, Siegbahn, *Phys. Zs.* xx. p. 533 (1919).
 73 Ta, Coster, *Zs. für Phys.* vi. p. 186 (1921).
 72 Hf, 69 Tm, Coster, *Phil. Mag.* xlvi. p. 956 (1923).
 71 Cp-57 La, Coster, *ibid.* xlv. p. 546 (1922).
 56 Ba-50 Sn, Coster, *ibid.* xliii. p. 1070 (1922).
- M-Emission lines 74 W-63 Dy, Hjalmar, *Zs. für Phys.* xv. p. 65 (1923).
 92 U-66 Dy, Stenström, *Dissertation Lund* (1919).
 74 W, Thoreus, *Zs. für Phys.* xxvi. p. 396 (1924).

TABLE VII.
The Values of Energy Levels (T/R).

	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	O_I	$O_{II, III}$	
74 W	893.0	850.6	752.1	208.1	191.3	169.8	138.3	133.7	44.1	38.0	33.0	18.8	18.4	2.9	2.8	5.7	5.2	74 W
73 Ta	832.2	820.8	728.0	199.5	183.2	162.9	132.2	127.8	41.2	35.3	30.9	17.8	16.6	2.2	1.9	4.7	4.4	73 Ta
72 Hf	832.0	791.3	704.5	191.8	175.9	156.9	126.6	122.6	40.0	34.0	29.8	16.8	16.0	1.6	1.4	4.8	4.3	72 Hf
71 Cp	802.6	762.9	681.2	183.8	168.6	150.9	120.9	117.2	36.9	32.5	28.7	16.1	14.7	1.0	0.7	4.2	4.0	71 Cp
70 Yb	774.6	735.4	659.2	177.1	162.2	145.8	116.4	112.8	36.2	31.0	27.5	14.9	14.2	0.9	0.6	—	3.6	70 Yb
69 Tm	746.8	708.8	637.3	170.3	155.5	140.2	111.7	108.4	34.4	30.0	26.6	14.5	13.2	0.9	0.4	—	3.8	69 Tm
68 Er	719.6	682.6	615.9	163.6	148.8	134.7	107.2	104.0	33.1	28.4	24.9	13.7	12.6	0.9	0.3	3.9	3.9	68 Er
67 Ho	693.2	657.1	594.7	157.1	142.7	129.3	102.7	99.8	31.8	26.9	23.8	12.8	12.0	0.8	0.2	—	2.7	67 Ho
66 Dy	667.7	632.2	574.2	151.2	136.9	124.5	98.5	95.8	31.0	26.1	23.2	12.2	11.6	—	—	3.1	3.2	66 Dy
65 Tb	642.6	608.3	553.9	145.0	131.0	119.6	94.2	91.6	29.4	24.3	21.0	11.4	11.1	—	—	3.5	2.6	65 Tb
64 Gd	618.2	584.6	533.9	139.0	125.5	115.0	90.0	87.7	28.6	23.0	20.4	10.7	10.8	—	—	4.0	3.3	64 Gd
63 Eu	594.3	561.5	514.4	133.1	120.2	110.3	86.0	83.8	27.2	22.6	20.4	10.7	10.4	—	—	3.6	2.9	63 Eu
62 Sm	571.2	538.9	495.0	127.2	114.7	105.8	81.9	79.9	25.9	20.9	19.5	10.0	9.8	—	—	3.1	2.8	62 Sm
60 Nd	526.2	495.5	457.8	116.5	104.8	96.8	74.2	72.5	23.7	19.2	17.8	9.2	9.2	—	—	3.1	2.7	60 Nd
59 Pr	504.3	474.6	439.6	111.6	99.3	92.4	70.3	68.9	22.7	18.3	16.9	8.9	8.7	—	—	3.1	2.3	59 Pr
58 Ce	483.3	454.1	421.9	106.2	94.6	88.1	66.7	65.4	21.7	17.4	16.2	8.4	8.5	—	—	3.2	2.5	58 Ce
57 La	462.9	434.2	404.4	100.7	90.0	84.0	62.9	61.7	20.5	16.5	15.4	7.8	7.8	—	—	3.0	2.3	57 La
56 Ba	441.9	414.3	386.7	95.4	84.6	79.0	58.8	57.6	18.8	14.9	14.0	6.9	6.9	—	—	3.1	2.0	56 Ba
55 Cs	421.8	394.9	369.3	89.8	79.3	74.4	54.6	53.6	17.1	13.6	12.6	5.9	5.7	—	—	1.9	1.7	55 Cs
53 I	382.6	357.6	336.0	79.2	69.1	64.8	46.8	45.9	14.0	9.4		4.1	4.1	—	—	—	0.7	53 I
52 Te	364.1	340.3	320.1	74.5	64.4	60.5	43.3	42.4	12.7	8.9		3.6	3.2	—	—	—	0.5	52 Te
51 Sb	346.1	323.6	305.3	70.4	60.0	56.4	40.4	39.7	12.1	7.2		3.3	3.2	—	—	0.8	0.1	51 Sb
50 Sn	329.4	306.3	289.5	65.3	56.2	53.1	36.5	35.9	10.2	7.1		2.0	1.9	—	—	0.2	0.6	50 Sn

TABLE VIII.
The Square Root of the Values of Energy Levels ($\sqrt{T/R}$).

	L _I	L _{II}	L _{III}	M _I	M _{II}	M _{III}	M _{IV}	M _V	N _I	N _{II}	N _{III}	N _{IV}	N _V	N _{VI}	N _{VII}	O _I	O _{II, III}	
74 W	29.883	29.166	27.425	14.43	13.83	13.03	11.76	11.56	6.64	6.17	5.75	4.34	4.28	1.71	1.67	2.38	2.29	74 W
73 Ta	29.862	28.630	26.982	14.13	13.54	12.76	11.50	11.31	6.42	5.94	5.56	4.21	4.08	1.50	1.39	2.18	2.10	73 Ta
72 Hf	28.844	28.130	26.541	13.85	13.26	12.53	11.25	11.07	6.32	5.83	5.46	4.09	4.00	1.24	1.19	2.19	2.08	72 Hf
71 Cp	28.831	27.620	26.101	13.56	12.98	12.28	11.00	10.82	6.08	5.70	5.36	4.01	3.84	1.0	0.8	2.04	2.01	71 Cp
70 Yb	27.831	27.118	25.675	13.31	12.74	12.08	10.79	10.62	6.02	5.57	5.24	3.86	3.77	1.0	0.8	—	1.90	70 Yb
69 Tm	27.327	26.622	25.245	13.05	12.47	11.84	10.57	10.41	5.87	5.47	5.16	3.81	3.64	1.0	0.7	—	1.94	69 Tm
68 Er	26.826	26.127	24.816	12.79	12.20	11.61	10.35	10.20	5.75	5.33	4.99	3.70	3.55	0.9	0.6	1.98	1.97	68 Er
67 Ho	26.328	25.634	24.387	12.53	11.94	11.37	10.14	9.99	5.64	5.19	4.88	3.57	3.46	0.9	0.4	—	1.63	67 Ho
66 Dy	25.840	25.144	23.963	12.29	11.70	11.16	9.93	9.79	5.57	5.11	4.81	3.49	3.41	0.9	—	1.77	1.79	66 Dy
65 Tb	25.349	24.664	23.534	12.04	11.45	10.94	9.70	9.57	5.42	4.93	4.69	3.37	3.33	—	—	1.87	1.61	65 Tb
64 Gd	24.864	24.179	23.107	11.79	11.20	10.73	9.49	9.36	5.34	4.80	4.59	3.32	3.29	—	—	2.00	1.81	64 Gd
63 Eu	24.379	23.697	22.679	11.54	10.97	10.50	9.27	9.15	5.21	4.76	4.51	3.27	3.22	—	—	1.88	1.69	63 Eu
62 Sm	23.899	23.214	22.249	11.28	10.71	10.28	9.05	8.94	5.08	4.57	4.41	3.16	3.14	—	—	1.75	1.68	62 Sm
60 Nd	22.939	22.260	21.335	10.79	10.24	9.84	8.61	8.52	4.87	4.39	4.22	3.03	3.03	—	—	1.76	1.66	60 Nd
59 Pr	22.456	21.785	20.967	10.57	9.96	9.61	8.39	8.30	4.77	4.27	4.12	2.98	2.96	—	—	1.75	1.51	59 Pr
58 Ce	21.984	21.310	20.511	10.30	9.72	9.39	8.17	8.09	4.66	4.17	4.02	2.89	2.92	—	—	1.79	1.57	58 Ce
57 La	21.514	20.837	20.108	10.03	9.49	9.17	7.93	7.86	4.53	4.06	3.92	2.79	2.79	—	—	1.72	1.52	57 La
56 Ba	21.022	20.355	19.664	9.77	9.20	8.89	7.67	7.59	4.34	3.86	3.74	2.63	2.62	—	—	1.75	1.43	56 Ba
55 Cs	20.537	19.872	19.218	9.47	8.90	8.62	7.39	7.32	4.14	3.68	3.55	2.43	2.40	—	—	1.4	1.3	55 Cs
53 I	19.566	18.916	18.329	8.90	8.31	8.05	6.84	6.78	3.74	3.07	3.07	2.01	2.02	—	—	—	0.8	53 I
52 Te	19.082	18.446	17.891	8.63	8.02	7.78	6.58	6.51	3.56	2.98	2.98	1.89	1.80	—	—	—	0.7	52 Te
51 Sb	18.605	17.988	17.472	8.39	7.74	7.51	6.36	6.30	3.47	2.69	2.69	1.81	1.78	—	—	0.9	0.4	51 Sb
50 Sn	18.143	17.500	17.016	8.08	7.50	7.29	6.04	5.99	3.19	2.66	2.66	1.41	1.37	—	—	0.5	0.7	50 Sn

By means of these data, the values of the spectral terms T divided by Rydberg's constant R and those of the square root of the same for different energy levels of each element were calculated, and are given in Tables VII. and VIII.* respectively. The levels M_I , M_{IV} , N_I , and N_{VI} may be computed in different ways, but those processes which involve the use of frequencies of the weaker and more diffuse emission lines as well as absorption edges were avoided, and the following formulæ were used:—

$$\begin{aligned} M_I &= L_{III} - L_{\alpha_1}, & M_{IV} &= L_{III} - L_{\alpha_2}, \\ N_I &= L_{III} - L_{\beta_6}, & N_{VI} &= L_{III} - L_{\alpha_2} - M_{\beta_7}. \end{aligned}$$

Just as in the paper by Bohr and Coster we plot the value $\sqrt{T}/R$ as a function of the atomic number Z , as shown in fig. 3, where, however, the L -curves have been omitted, owing to the very large values of their energy levels. In the figure the black dots represent the levels with odd suffixes and the white circles those with even suffixes. In the case of the L - and M -levels the points lie on smooth curves, which have distinct and sudden bends at La (57) and Cp (71), a feature which was emphasized by Bohr and Coster and which will be discussed later. On the other hand, the points corresponding to the N - and O -levels have small irregularities. This is perhaps due to the fact that the term values here, which are obtained by the difference between absorption and emission frequencies, are small, and consequently the errors of both these measurements are revealed more prominently than in the case of the L - and M -levels.

In this connexion the following remarks as regards the accuracy of term values may be made. First of all we have the error in the measurements of the L -absorption spectra. This has been already pointed out and is rather large for L_I . The values of the other levels are calculated from the frequencies of the L -absorption edges by means of L - or M -emission lines, some of which are weak and diffuse, for instance, L_{α_1} , L_{β_6} , and L_{β_7} †. Thus the errors in the values of some levels are fairly high, and we may consider them generally twice as large as those in the L -absorption edges. Especially as regards the L_{β_7} line, which is used for the calculation of the O_I -level, there are some uncertainties in

* Some values which were improved by the further measurements of the present writer are given differently in these tables from those in our previous work. The difference is, however, in most cases within the limit of the experimental error.

† As regards the accuracy of emission lines, see Coster, *Phil. Mag.* xliii. p. 1084 (1922).

its identification in the case of certain elements*, because this weak line lies quite close to another weak line and even crosses it, if we follow from one element to another. This may perhaps account for the irregularity of the values of the O_I -levels. But, of course, we cannot draw any definite conclusion as to the certainty of the explanation of this and other irregularities without a further accurate test, and especially without a closer systematic investigation of the emission lines. The writer is at present occupied with such an investigation.

At the end of this paragraph another remark may be added that the frequency of absorption edges, as is well known now, is influenced by the chemical and physical state under which the element in question exists. The maximum difference is about 1.0 unit in frequency between different compounds for the K-absorption of P, S, Cl †, Ti, Va, Cr, and Mn, and the L-absorption of Sn, Sb, Te, and I ‡. As mentioned above, the present experimental results were obtained with different sorts of compounds for the different elements. The tables given above consequently contain uncertainties as to their absolute values to the extent that they give the values obtained not with pure elements, but with compounds. But from the results we may conclude that the general features of the curves, which are of primary importance and will be discussed in the next paragraph in connexion with the natural system of the elements, is not thereby materially affected.

Discussion of the Results.

Following the classification adopted by Bohr and Coster, each level in fig. 3 is characterized by a symbol $n(k_1, k_2)$, where k_2 is either equal to k_1 or equal to $k_1 - 1$. The appearance of any such level is assumed to be conditioned by the presence in the normal atom of electronic orbits for which the principal quantum number is equal to n , and for which the azimuthal quantum numbers are equal to k_1 and k_2 . Any pair of levels for which the values of n and k_1 are the same, whereas the values of k_2 differ by one unit, form a so-called relativity doublet. For such doublets the distance between the corresponding curves increases in general

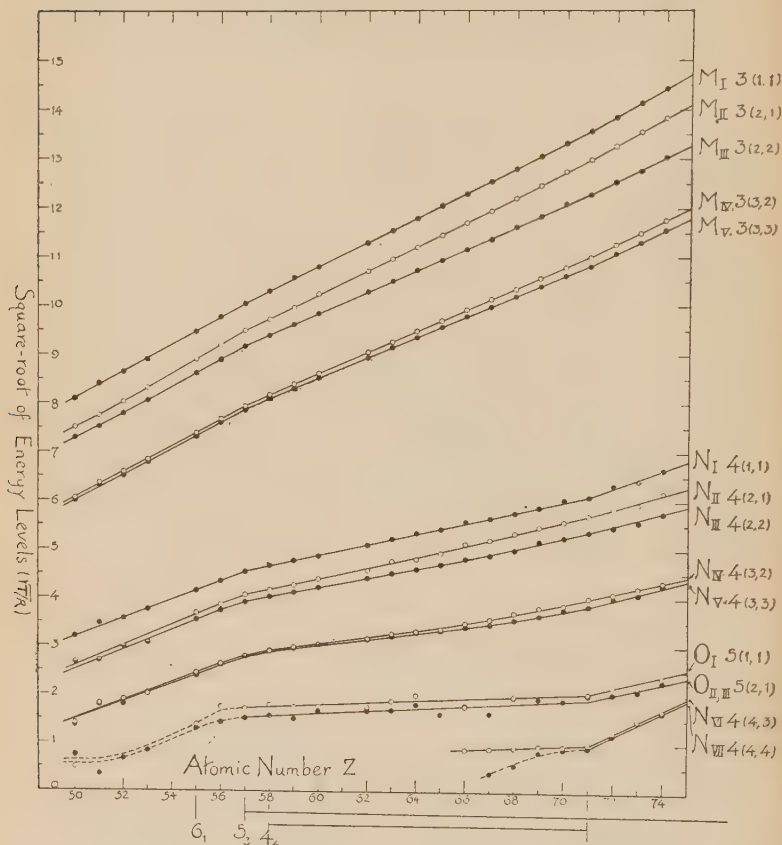
* This was kindly pointed out by Dr. D. Coster during the preparation of this paper. Compare Coster, Phil. Mag. xliv. p. 554 (1922).

† Lindh, Dissertation Lund (1923).

‡ Coster, Zs. für Phys. xxv. p. 83 (1924). Tandberg, Arkiv för Matematik, Astronomi och Fysik, xviii. no. 14, p. 1 (1924).

rapidly with the atomic number. Pairs of levels for which n and k_2 are equal, but for which k_1 differs by one unit, form the so-called screening doublets, which show themselves by the remarkably parallel course of their curves. The theoretical explanation of these features of the curves

Fig. 3.



presents at present unsolved problems, for the discussion of which the reader is referred to the paper by Bohr and Coster. Here we shall confine ourselves to a discussion of those properties of the curves which may be brought in direct connexion with the gradual development of the electronic groups due to the appearance of orbits of new types with increasing atomic number. The addition of such new orbits can be traced partly by the appearance of new

X-ray levels, and partly by changes in the rate of variation with the atomic number of levels already present. Within the region of elements investigated in this paper we shall, according to Bohr's theory, expect the first appearance of 6_1 orbits at Cs (55), of 5_3 orbits at La (57), and of 4_1 orbits at Ce (58). Now, the orbits of the 6_1 type correspond within the whole sequence of elements under consideration only to valence electrons moving for the most part in the exterior region of the atom, and it is therefore easily understood that it has not been possible with certainty to detect the appearance of the corresponding new levels or to recognize any marked influence on the other levels due to the addition of such orbits. With the 4_1 orbits the situation is quite different. Their appearance in the atom marks the final states of completion of the 4-quantum group, and according to the theory gives rise to the presence of the family of rare earths within the periodic table. As mentioned, Bohr and Coster drew attention to a number of anomalies in the course of the level curves in the region of this family of elements which could all be accounted for on the basis of the theoretical expectation that the added 4-quantum orbits will find their position in a region of the atom closer to the nucleus than that region where the electrons in 5- and 6-quantum orbits are moving during the greater part of their revolutions. The present measurements allow us to examine these anomalies with greater accuracy, and to obtain a general support of the conclusions of Bohr and Coster.

In conformity with the classification of fig. 3, the levels which are directly conditioned by the presence of electrons in 4_1 orbits are N_{VI} and N_{VII} . According to the theory, the stage in the development in the 4-quantum group, to which the binding of electrons in such orbits gives rise, is initiated in Ce (58) and is completed in Cp (71), which forms the last of the rare earth elements. This development takes place, so to speak, in competition with the binding of the valence electrons; and we must therefore expect that as long as it goes on, the work necessary to remove a 4_1 electron from the atom will remain quite small, about the same order as that for valence electrons 6_1 and smaller than that for 5_1 and 5_2 electrons, throughout the whole rare earth family, and first start to increase steadily at the element Hf (72). This is brought out clearly in the course of the N_{VI} and N_{VII} curves, which show a sharp upwards bend at Cp (71). As we know from older measurements, these curves will cross the O-curves somewhere between Ir (77) and Tl (81). As indicated in the figure, the curve N_{VII} below Cp (71)

seems to diverge from the N_{VI} curve. This is quite unusual because these two curves form what is called a relativity doublet; the divergence, however, seems to be too large to be explained by systematic experimental errors. Whether this anomaly has real existence, and points to special features connected with the development of the 4-quantum group, remains, however, to be settled.

As regards the other levels, the influence of the development of the 4-quantum group is perhaps most strikingly shown in the O-levels. The irregularities in the points representing the measurements are in this case probably due to accidental errors, but the figure nevertheless brings out clearly that these levels during the whole region of the rare earth family remain very nearly constant. This is explained, according to the theory, by the circumstance that the added 4_1 electrons will move in a region of the atom lying within the region in which the 5_1 and 5_2 electrons move during the greater part of their revolutions. The effect of the increasing nuclear charge on the strength of binding of these electrons will therefore in the interval between La (57) and Cp (71) be nearly balanced by the screening of the added electrons in the 4-quantum orbits. The O_I - and $O_{II, III}$ -curves have, furthermore, a distinct bending at Ba (56) instead of La (57), at which all other curves have a marked bend, although there seems to be a very slight indication of bending at Ba (56) for some levels. This unique feature of the O-levels is perhaps caused by the first binding of the 5_3 -electron at La (57), the effect of which will not be so much felt by other levels as by the 5-quantum orbits.

Apart from small anomalies probably due to accidental errors, the levels N_I , N_{II} , N_{III} , N_{IV} , and N_V , which are conditioned by the presence of 4_1 , 4_2 , and 4_3 orbits, show a smooth course with a distinct bend at La (57) and a less pronounced bending at Cp (71). On the theory this is accounted for by the diminishing influence on the strength of binding of these electrons, due to the repulsive forces from the 4_1 electrons, which move in the same region in the atom as the 4_1 , 4_2 , and 4_3 electrons, and which are just added in the interval between La (57) and Cp (71). Attention may be called to various systematic deviations in the relationship between neighbouring N-curves from what is usually expected from the behaviour of relativity and screening doublets. For instance, the curves N_{IV} and N_V seem to draw closer after Hf (72), and there is an indication that the N- and O-curves show certain irregularities below

FIG. 1 *a*.—H α L $_{III}$.

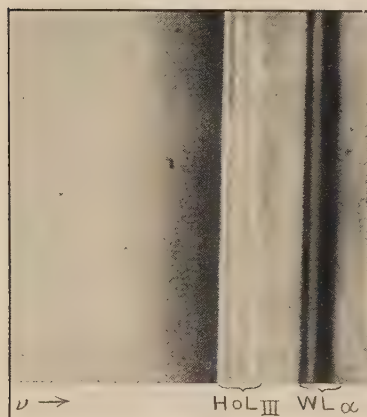
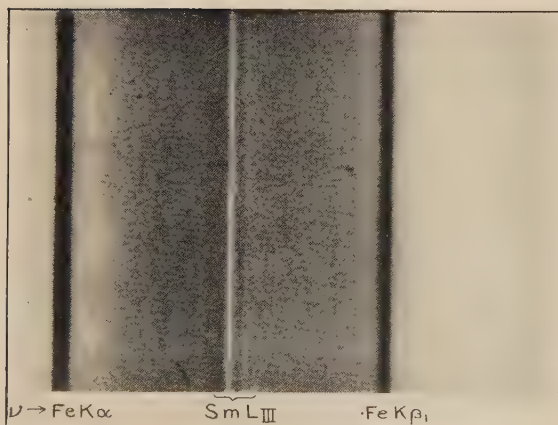
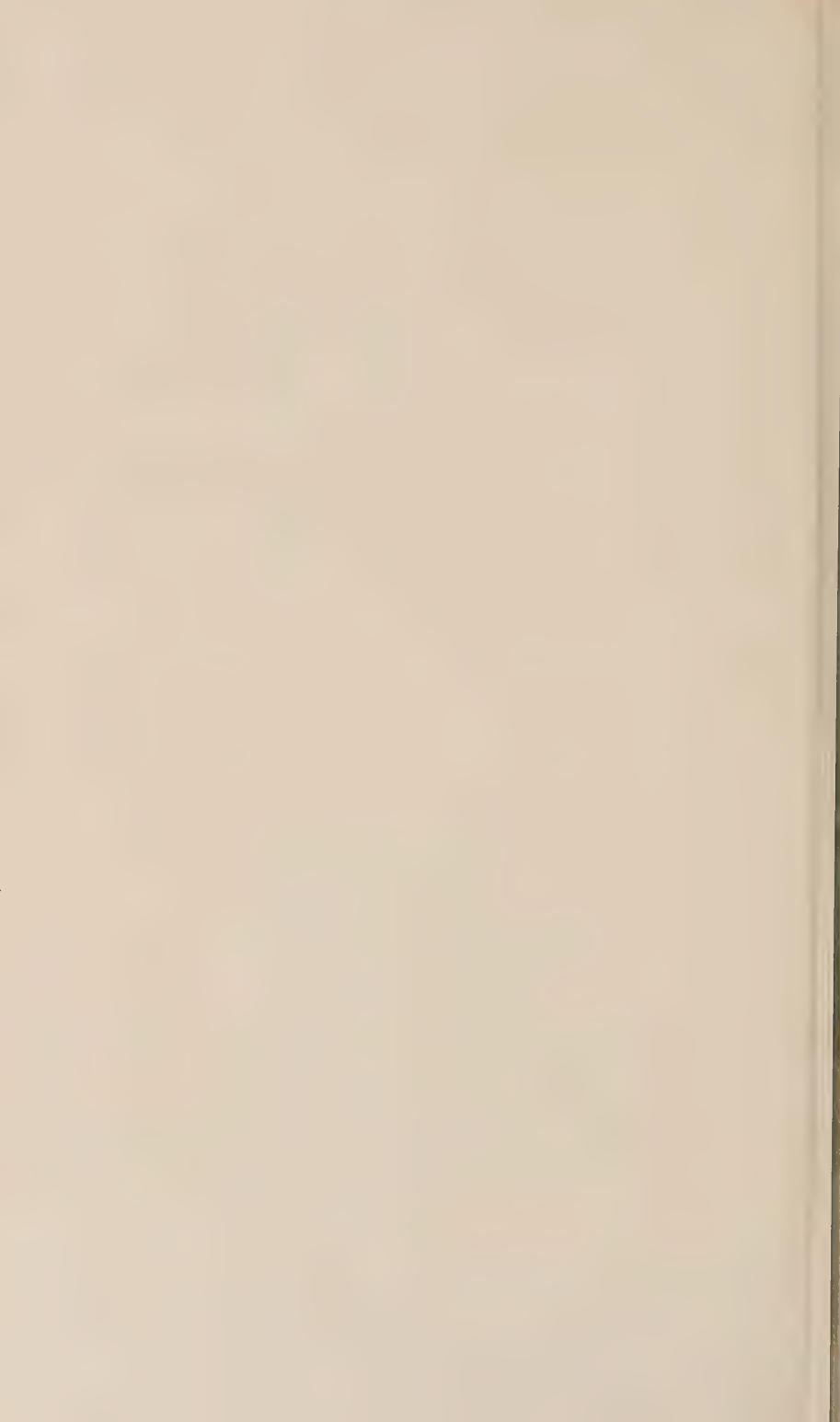


FIG. 2 *a*.—SmL $_{III}$.





X (54), which are perhaps to be connected with the development of the 5-quantum groups which are brought to partial completion at X (54). Whether these facts represent the real nature of things or come merely from the experimental errors, it is difficult to decide at present.

The development of the 4-quantum group can, moreover, be clearly traced in the M-levels, since all the curves representing these levels show bends at La (57) and Cp (71). The M-levels are conditioned by electrons in 3-quantum orbits moving still closer to the nucleus than the 4-quantum electrons. In the effect under consideration we have to do with what is denoted by Bohr and Coster as the outer screening effect, which arises from the balancing influence on the work necessary to remove a 3-quantum electron, due to the increase in the strength of the binding of the electrons in the 4-quantum orbits resulting from this removal.

In conclusion, the author wishes to thank Professor N. Bohr for his constant encouragement during the experiment, and for his invaluable discussion and criticism during the preparation of this paper. His thanks are also due to Dr. D. Coster for his unfailing kindness in giving instructive advice throughout the work.

Universitetets Institut for teoretisk Fysik,
Copenhagen, November 1924.

LIX. *The Motion of Free Electrons in Black Body Radiation, and the Interaction between Radiation and Matter.* By G. BREIT*.

Introduction.

THE motion of free electrons in black body radiation has been discussed by Fokker†, who showed that if the waves constituting black body radiation have random phases, the mean kinetic energy of the electron's motion is not $3/2kT$ but about $1/24$ of this value. The problem has been considered again by Pauli‡, who discusses the motion of electrons on the supposition that quanta are absorbed bodily by electrons and that simultaneously with the (absorption) of a quantum $h\nu$ a momentum $-h\nu/c$ is (emission) (absorbed) by the electron. Pauli obtains $3/2kT$ for the (emitted)

* Communicated by the Author.

† Dissertation Leiden, 1913; *Arch. Néerl.* (3 a) iv. p. 379 (1918).

‡ *Zeits. f. Phys.* xviii. p. 273.

mean kinetic energy. It is generally supposed that $3/2kT$ is the proper value for the mean kinetic energy of free electrons in black body radiation, and the present situation is therefore such as to condemn the classical wave theory in favour of the light-dart theory from considerations based on the motion of free electrons alone.

This evidence in favour of light darts is re-examined below. In § 1 the problem of the statistical equilibrium of free electrons is considered as a special case of a coupled quantized system, and the *a priori* necessity of having the mean kinetic energy equal to exactly $\frac{3kT}{2}$ is questioned.

In § 2 it is shown that Fokker's treatment is concerned only with one type of motion, which may be termed the slow surging or progressive type. In addition to this, there is a rapidly vibratory type. A numerical estimate of its value shows it to be small at ordinary temperatures. It is pointed out that Fokker's result must be modified if there are systematic phase relations between the waves constituting the radiation. Reasons are given for looking at the term ρ^2/ν^2 in the numerator of Fokker's result as a special case of $\alpha\bar{\epsilon}^2/h$, where $\bar{\epsilon}^2$ is Einstein's expression for the average square of the fluctuation of energy density applied to unit volume, which for Planck's formula has the expression $h\nu\rho + h\rho^2/\alpha\nu^2$ and for the Rayleigh-Jeans relation degenerates into $h\rho^2/\alpha\nu^2$. It is shown that with this change Fokker's formula gives exactly $3/2kT$ for the mean kinetic energy of free electrons.

In § 3 the meaning of the modification introduced in § 2 is examined, and statistical relations are derived which must be satisfied in order to make the modification valid.

In § 4 the problem is discussed from the point of view of very loosely bound electrons, and it is shown that the case is not essentially distinct from the case of Bohr atoms such as are discussed by Einstein*, and the writer's remarks† applied to Bohr's atoms are translated into corresponding statements for free electrons. It is shown that for both problems the essential condition is that the relation between the electric force on the electron (which does the work) and the motional force due to the magnetic intensity (which gives the radiation pressure) should be the same as on the classical theory. This suggests thinking of the transmission of energy and momentum in terms of old-fashioned waves, and regarding the absorbed energy as *force* $\times$ *distance* where

* Einstein, *Phys. Zeitschr.* xviii. p. 121 (1917).

† G. Breit, *Phys. Rev.* pp. 313-319 (1923).

the force is the force due to the wave and the distance is closely allied to the actual distance traversed by the electron. Similarly, the momentum imparted by the wave is calculable from the motional intensity $\frac{e}{c} [\mathbf{v}, \mathbf{h}]$, where $\mathbf{v}$ is taken for the same motion which is considered in the calculation of the absorbed energy. This motion is shown presently to be not exactly the electronic motion, but to be more closely allied with Bohr's corresponding motion.

In § 5 the difficulty of applying the wave theory to the photoelectric effect is discussed, and it is shown that the difficulty disappears if the absorption is conceived of on the lines of § 4. The present point of view differs from the older in looking at the absorbed energy as *force* $\times$ *distance* instead of considering the flux of Poynting's vector across a section of the wave of atomic dimensions. The Principle of Conservation of energy is shown to be satisfied by the postulated mechanism. It is shown that the view proposed may be looked at as a generalization of Bohr's Principle of Correspondence, provided the action of the radiation force $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$ on the atom is *unclassical* to the same extent as the action of the external wave. The *unclassical* nature of both consists in a cumulative action on the atom for a time long in comparison with the period of the wave without affecting the motion of the *equivalent corresponding* mechanism, which is an harmonic oscillator of a frequency equal to the emission frequency and of an amplitude equal to a mean amplitude of the motion of the electron between the two states. The integral actions, however, are the same as on the classical theory. This is in agreement with phenomena of dispersion. The view proposed also explains the very high absorption of γ rays by the atom in which the γ rays have been produced, which is found from a study of γ -ray spectra by Ellis and Meitner.

§ 1. The problem of free electrons subjected to the action of black body radiation is a special case of the general problem of investigating the result of the action of a system (A) on a system (B). [The system (A) is the radiation. The system (B) is the electron.] The essential characteristic of our case is that the number of degrees of freedom in (A) is large and that in (B) is small. The approximation which is made by Fokker in the problem of free electrons, and which has always been made by everyone in the problem of resonators and atoms, is that one can

regard the motion of (A) as unaffected by (B), and from the statistically known state of (A) calculate the so far statistically unknown state of (B). If on using the Planck radiation formula the classical interactions do not give the correct mean kinetic energy for free electrons (B), then one must conclude that the interactions between (A) and (B) are not classical. This is the claim made for the special case of free electrons from Fokker's calculation by Pauli.

The cornerstone of this line of reasoning is the necessity of having the mean kinetic energy of (B) equal to $3/2kT$, which is the value it would have if it were not coupled to (A). The necessity for this is not at all obvious. As soon as an interaction between (A) and (B) is introduced, we cease to have two separate systems, and we must deal with a coupled system. In this any of the old coordinates of (A) implies something as to the state of (B), and *vice versa* *.

From a purely formal point of view we must quantize the coupled system and apply quantum statistics to the result. If the motion of the coupled system (AB) is multiply periodic, this can always be done. In the very process of quantization the interactions between (A) and (B) are of necessity taken as classical. From this point of view it seems more proper to question the validity of the statement that the mean kinetic energy of a "free" electron is $3/2kT$ rather than the classical nature of the interactions, because the unclassical element comes in through the quantization of the coupled system (AB) and not through the unclassical nature of the interactions. The view maintained here is that an electron put in black body radiation cannot be properly called *free* because it is coupled to the radiation.

The fact that the radiation force $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$ is known to be inapplicable to the Bohr atom is, of course, an objection to the formal viewpoint just sketched. So far as the problem of free electrons is concerned, we can imagine a fictitious system in which a dissipative force $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$ is operative for the electron and in which an equal and opposite reaction is exerted on the rest of the system in such a way as to keep the resultant system conservative.

* Jeans, in his papers: Phil. Mag. xviii. p. 209 (1909), xvii. p. 773 (1909), xxvii. p. 14 (1914), deals with the interaction of free electrons with radiation. However, he does not discuss the radiation pressure effects.

Even though we cannot accept without further proof the necessity for having $\frac{1}{2}mv^2 = \frac{3}{2}kT$ for electrons in black body radiation, we have some reason for expecting that electrons emerging by chance from a space occupied by black body radiation into free space should satisfy this condition. It may be shown that it is probable that Fokker's calculation deals with that part of the motion which survives after the escape of the electron.

The approximate assumption which is very conveniently made by Fokker is that the motion of (A) is not modified appreciably by the presence of (B). This amounts to saying that the coupling between (A) and (B) is loose. The problem of loosely-coupled systems has been considered by Burgers*, who showed that the quantizations become independent, and that the perturbations are in the limit calculable on a purely classical basis. From this point of view it is again questionable that the apparent violation of statistical mechanics is to be attributed to the classical interactions.

§ 2. The motion of an electron in the radiation field is thought of most simply by depriving it of some of its degrees of freedom. To start with, let us constrain the electron to move in a straight line. The calculation of $\frac{1}{2}mv^2$ is very clear in this case. We consider a very long period of time T , and resolve the component of the electric intensity along the line of motion into a Fourier series with T as period. If T is very great, the effects of the initial motion are of no importance and the electron may be thought of as executing forced vibrations under the action of each of the terms in the expansion of the electric intensity. Using the Heaviside-Lorentz notation, the equation of motion is

$$m\ddot{x} - \frac{e^2}{6\pi c^3} \ddot{x} = e d_x, \quad . \quad . \quad . \quad (1)$$

from which it can be shown that the mean kinetic energy is for Planck's radiation formula

$$\frac{m\overline{\dot{x}^2}}{2} = \frac{1}{\pi} \int_0^\infty \frac{mh\nu d(e^2\nu/(3c^3))}{\left(e^{\frac{h\nu}{kT}} - 1\right) \left(m^2 + \left(\frac{e^2\nu}{3c^3}\right)^2\right)} \quad . \quad . \quad (2)$$

If in this formula $h \rightarrow 0$, $\frac{m\overline{\dot{x}^2}}{2} \rightarrow \frac{kT}{2}$. This means that for

* Burgers, Dissertation Leiden, p. 216; *Versl. Akad. Amst.* xxvi. p. 702 (1917).

the Rayleigh-Jeans radiation $\frac{kT}{2}$ is obtained. However, for ordinary temperatures the value of the expression on the right is only a very small fraction of $\frac{kT}{2}$, for its order of magnitude is that of $kT \tan^{-1} \left(\frac{e^2 \nu}{3mc^3} \right)$, where $\nu \approx \frac{kT}{\hbar}$. If $\nu = 10^{15}$, the energy of the motion is only about $10^{-7} kT$.

If the energy of the electron having one degree of freedom had to be $\frac{kT}{2}$, the calculation of Fokker would be unnecessary, for the above simple formula gives less than the required value. An inspection of the above formula shows, however, the presence of the factor $x/(e^x - 1)$, ($x = h\nu/kT$), so familiar in the quantum theory of specific heats. The reason why the kinetic energy is too small is that the electron is to be considered as coupled to the radiation, and that its motion is to be thought of as resolved into harmonic vibrations each of which is associated with a general mode of vibration of the coupled system as a whole (§ 1). The small value of the vibratory energy of the electron is in this case a natural consequence of the small value of the vibratory energy of the higher frequencies in the black body spectrum. The small value is not in contradiction with the statistical requirement that free electrons having Maxwell's distribution—then subjected to the action of black body radiation, and then removed from the radiation—should remain with Maxwell's distribution. For there are no radiation pressure-effects on the constrained electron, and the vibratory motion is so small that the electron has a negligible chance of leaving the radiation field.

The type of motion illustrated by the constrained electron is thus seen to be powerless for giving a criterion in favour of or against light-darts. It is not the type considered by Fokker.

We suppose next that the line of constraint OX is allowed to move perpendicularly to itself in the plane OXY. We imagine the line endowed with a mass $-m + M \gg m$. The equations of motion are :—

$$\left. \begin{aligned} m\ddot{x} - \frac{e^2 \ddot{x}}{6\pi c^3} &= e(d_x + \dot{y}h_z/c), \\ M\ddot{y} - \frac{e^2 \ddot{y}}{6\pi c^3} &= e(d_y - \dot{x}h_z/c). \end{aligned} \right\} \quad \dots \quad (3)$$

If M is very great, the values of $\dot{y}$ are very small. As a first approximation, we may consider the vibratory motion of x to depend on d_x . To this approximate value of x there corresponds a value of $\dot{x}$ which, when substituted into the second of the two equations (3), gives rise to surging motions of y (due essentially to combination-frequency terms arising from $-\dot{x}h_z/c$). These are the terms taken into account by Fokker. Making the calculation for three degrees of freedom, and assuming that this involves the addition of the effects due to each, he gets a result equivalent to

$$\frac{1}{2}mv^2 = \frac{3c^3}{64\pi} \frac{\int_0^\infty \frac{\rho^2}{v^2} dv}{\int_0^\infty \rho dv}, \quad . \quad . \quad . \quad . \quad (4)$$

where $\rho(v)dv$ is the energy density in the frequency range dv , which on substituting Planck's expression for ρ becomes

$$\frac{1}{2}\overline{mv^2} = \frac{3}{8}kT \frac{\int_0^\infty \frac{x^4}{(e^x-1)^2} dx}{\int_0^\infty \frac{x^3}{e^x-1} dx} = \frac{3}{2}kT \times 0.0417. \quad . \quad (4')^*$$

Formula (4) Fokker derives from his equation

$$\frac{1}{2}\overline{mv^2} = \frac{\overline{X^2} + \overline{Y^2} + \overline{Z^2}}{4Q\tau},$$

in which (X, Y, Z) is the momentum imparted to the electron by the electromagnetic radiation in time τ , and Qv is the systematic resisting force exerted by the radiation on an electron moving with velocity v . The numerator in (4) is thus essentially

$$\frac{X^2}{\tau} = \frac{2}{9} \left(\frac{e^2}{4\pi mc} \right)^2 \int_0^\infty \frac{\rho^2}{v^2} dv,$$

while the denominator is

$$4Q = \frac{4e^4}{6\pi c^5 m^2} \int_0^\infty \left(-v \frac{\partial \rho}{\partial v} + \rho \right) dv = \frac{2}{9} \frac{4e^4}{\pi c^5 m^2} \int_0^\infty \rho dv \dagger.$$

* h is seen to be absent in this formula. This in itself raises a suspicion as to its validity.

† This transformation is valid only if $v\rho$ vanishes both at $v=\infty$ and at $v=0$. Thus the transformation is not applicable in the case of the formula of Rayleigh-Jeans.

The term $4Q$ is obtained by considering the reaction on the electron due to the radiation in a very long time during which the electron moves with finite average velocity. The problem is essentially that of forced vibrations and of transforming the radiation field to a moving system of reference. There is thus little reason for doubting the expression for $4Q$.

The origin of $\bar{X}^2/\tau$ is, in cross-product terms,

$$\frac{1}{\tau} \left(\frac{e^2}{2\pi m \nu} \sum_{1,2} \int_t^{t+\tau} [\mathbf{d}_1, \mathbf{h}_2]_y dt \right)^2^*,$$

where $(\mathbf{d}_1, \mathbf{h}_1)$, $(\mathbf{d}_2, \mathbf{h}_2)$ are the electric and magnetic intensities in two waves of neighbouring frequencies, and $[\]$ denotes the vector product. If there are no phase relations between the various waves, the product terms between the various terms in the summation for $\bar{X}^2/\tau$ need not be taken into account. They are actually neglected by Fokker.

Now, it is known that Einstein's fluctuation formula

$$\bar{\epsilon}^2 = h\nu\rho + h\rho^2/(\alpha\nu^2)$$

is inconsistent with a picture of black body radiation based on waves with random phase differences †. We must admit, therefore, the possibility of some phase relations in a manner similar to Planck's ‡.

Since the numerator of (4) contains ρ^2/ν^2 just as the classical part of $\bar{\epsilon}^2$, and since the origin of $\bar{X}^2/\tau$ is closely similar to the origin of $\bar{\epsilon}^2$ (one arising from Poynting's vector and the other from the energy density), we may provisionally expect that the contribution to $\bar{X}^2/\tau$ due to the frequency range $d\nu$ is changed by taking into account the phases in the same proportion as $\bar{\epsilon}^2$ is changed. This ratio is

$$1 + \alpha\nu^3/\rho = e^x, \quad (x = h\nu/kT).$$

Hence, from (4'),

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{8} kT \cdot \frac{\int_0^\infty x^4 e^x (e^x - 1)^2 dx}{\int_0^\infty \frac{x^3}{e^x - 1} dx} \S = \frac{3}{2} kT. \quad (5)$$

* See equation (7) below.

† H. A. Lorentz, 'Les Théories Statistiques en Thermodynamique.' (Teubner, 1916.)

‡ M. Planck, *Ann. der Phys.* lxxiii. p. 272 (1924).

§ $4 \int_0^\infty \frac{x^3}{e^x - 1} dx = - \int_0^\infty x^4 \frac{d}{dx} \left(\frac{1}{e^x - 1} \right) dx = \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx.$

To summarize this paragraph, the numerator of Fokker's formula (4) must be modified if the waves of the radiation are to conform with the thermodynamically derivable expression $\bar{\epsilon}^2$ of Einstein. Regarding the changes in $\bar{\epsilon}^2$ and in $\bar{X}^2/\tau$ as proportional to each other, Fokker's result becomes equal to $3/2kT$.

§ 3. We must now inquire into the meaning of the hypothesized equivalence of the effects of phase relations on $\bar{X}^2/\tau$ and on $\bar{\epsilon}^2$.

Let us calculate $\bar{\epsilon}^2$. We consider the radiation field inside a sphere. The energy density is given by $\frac{1}{2}(d^2 + h^2)$. The value of d at any point is the sum of the values due to the various component waves. The value of ϵ which we must consider is therefore

$$\epsilon = \sum (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) \iiint_S \cos 2\pi \left(\nu_1 t - \frac{l_1 x + m_1 y + n_1 z}{\lambda_1} - \psi_1 \right) \\ \times \cos 2\pi \left(\nu_2 t - \frac{l_2 x + m_2 y + n_2 z}{\lambda_2} - \psi_2 \right) dx dy dz,$$

where $\mathbf{d}$, $\mathbf{h}$ are vector amplitudes; ν , λ , (l, m, n) , ψ are the frequency, wave-length, direction cosines, and phase of each wave; and where the integration is extended over the interior of the sphere. The summation is extended over all combinations (1, 2), each combination being taken once. We have, on performing the integration,

$$\frac{1}{3} \frac{\epsilon}{4\pi r^3} = \sum \frac{1}{2} (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right) \\ \times \cos 2\pi ((\nu_1 - \nu_2)t - \psi_1 + \psi_2) \\ + \sum \frac{1}{2} (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) \left(\frac{\sin x'_{12}}{x'_{12}^3} - \frac{\cos x'_{12}}{x'_{12}^2} \right) \\ \times \cos 2\pi ((\nu_1 + \nu_2)t - \psi_1 - \psi_2)^*,$$

where

$$x_{12} = 2\pi r \sqrt{\left(\frac{l_1}{\lambda_1} - \frac{l_2}{\lambda_2}\right)^2 + \left(\frac{m_1}{\lambda_1} - \frac{m_2}{\lambda_2}\right)^2 + \left(\frac{n_1}{\lambda_1} - \frac{n_2}{\lambda_2}\right)^2}, \\ x'_{12} = 2\pi r \sqrt{\left(\frac{l_1}{\lambda_1} + \frac{l_2}{\lambda_2}\right)^2 + \left(\frac{m_1}{\lambda_1} + \frac{m_2}{\lambda_2}\right)^2 + \left(\frac{n_1}{\lambda_1} + \frac{n_2}{\lambda_2}\right)^2}.$$

* We disregard $\sum \frac{d^2 + h^2}{4} \left(\frac{\sin x}{x^3} - \frac{\cos x}{x^2} \right) \cos 4\pi(\nu t - \psi)$ because phase relations introduced by these terms do not appear likely to give systematic effects. However, there is a possibility of there being a need of taking these into account.

Squaring the above relation and averaging, we obtain

$$\begin{aligned}
 \overline{\left(\frac{\epsilon}{4\pi r^3/3}\right)^2} &= \frac{1}{8} \sum (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) \left\{ \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right)^2 \right. \\
 &\quad \left. + \left(\frac{\sin x'_{12}}{x'_{12}^3} - \frac{\cos x'_{12}}{x'_{12}^2} \right)^2 \right\} \\
 &+ \frac{1}{4} \sum_{\nu_1 - \nu_2 = \nu_3 - \nu_4} (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) (\mathbf{d}_3 \mathbf{d}_4 + \mathbf{h}_3 \mathbf{h}_4) \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right) \\
 &\quad \times \left(\frac{\sin x_{34}}{x_{34}^3} - \frac{\cos x_{34}}{x_{34}^2} \right) \cos 2\pi(\psi_1 - \psi_2 - \psi_3 + \psi_4) \\
 &+ \frac{1}{4} \sum_{\nu_1 + \nu_2 = \nu_3 + \nu_4} (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) (\mathbf{d}_3 \mathbf{d}_4 + \mathbf{h}_3 \mathbf{h}_4) \left(\frac{\sin x'_{12}}{x'_{12}^3} - \frac{\cos x'_{12}}{x'_{12}^2} \right) \\
 &\quad \times \left(\frac{\sin x'_{34}}{x'_{34}^3} - \frac{\cos x'_{34}}{x'_{34}^2} \right) \cos 2\pi(\psi_1 + \psi_2 - \psi_3 - \psi_4) \\
 &+ \frac{1}{4} \sum_{\nu_1 - \nu_2 = \nu_3 - \nu_4} (\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2) (\mathbf{d}_3 \mathbf{d}_4 + \mathbf{h}_3 \mathbf{h}_4) \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right) \\
 &\quad \times \left(\frac{\sin x'_{34}}{x'_{34}^3} - \frac{\cos x'_{34}}{x'_{34}^2} \right) \cos 2\pi(\psi_1 - \psi_2 - \psi_3 + \psi_4). \quad (6)
 \end{aligned}$$

The first summation gives rise to the term $h\rho^2/(\alpha\nu^2)$ in ϵ^2 . In fact, the space positions of the wave normals 1 and 2 are entirely random. Further, the average value of $(\mathbf{d}_1 \mathbf{d}_2 + \mathbf{h}_1 \mathbf{h}_2)^2$ for two waves, the normals of which form a fixed angle θ but which have random polarizations, is

$$\frac{1}{2}(1 + \cos \theta)^2(\overline{d_1^2})(\overline{d_2^2}),$$

as may be shown by integration.

The first summation is then

$$\begin{aligned}
 \frac{1}{16} \sum (\overline{d^2})^2 &\left\{ (1 + \cos \theta)^2 \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right)^2 \right. \\
 &\quad \left. + (1 + \cos \theta)^2 \left(\frac{\sin x'_{12}}{x'_{12}^3} - \frac{\cos x'_{12}}{x'_{12}^2} \right)^2 \right\}.
 \end{aligned}$$

The space averages in either of the terms are taken by assigning to the interval $(\theta, \theta + d\theta)$ the probability $\frac{1}{2} \sin \theta d\theta$.

Setting

$$2\pi r/\lambda = N,$$

we have

$$x_{12}^2 = N_1^2 + N_2^2 - 2N_1 N_2 \cos \theta.$$

Thus

$$\begin{aligned} & (1 + \cos \theta)^2 \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right)^2 \\ &= \frac{1}{2} \int_{\cos \theta = -1}^{+1} \left(1 + \frac{N_1^2 + N_2^2 - x_{12}^2}{2N_1 N_2} \right)^2 \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right)^2 d(\cos \theta) \\ &= \frac{1}{2N_1 N_2} \int_{|N_1 - N_2|}^{N_1 + N_2} \left(1 + \frac{N_1^2 + N_2^2 - x^2}{2N_1 N_2} \right)^2 x \left(\frac{\sin x}{x^3} - \frac{\cos x}{x^2} \right)^2 dx. \end{aligned}$$

Here we need to take into account only the lowest power in $1/N$. With a sufficient approximation, the integral is

$$\frac{2}{N^2} \int_{|N_1 - N_2|}^{N_1 + N_2} x \left(\frac{\sin x}{x^3} - \frac{\cos x}{x^2} \right)^2 dx,$$

which is easily shown by partial integrations to be
[on neglecting $\frac{1}{|N_1 + N_2|}$]

$$\frac{1}{2N^2} \left\{ \frac{\sin^2(N_1 - N_2)}{(N_1 - N_2)^2} + \left(\frac{\sin(N_1 - N_2)}{(N_1 - N_2)^2} - \frac{\cos(N_1 - N_2)}{N_1 - N_2} \right)^2 \right\}.$$

The average of the second term is similarly found to be zero. The contribution to the first summation in (b) to ϵ^2 is then

$$\begin{aligned} (\bar{\epsilon}^2)_1 &= \frac{9}{32} \left(\frac{4\pi r^3}{3} \right)^2 \sum \frac{(d_1^2)(d_2^2)}{N^2} \left\{ \frac{\sin^2(N_1 - N_2)}{(N_1 - N_2)^2} \right. \\ &\quad \left. + \frac{\sin(N_1 - N_2)}{(N_1 - N_2)^2} - \frac{\cos(N_1 - N_2)}{N_1 - N_2} \right\}. \end{aligned}$$

Here

$$\sum_{d\nu} \bar{d}^2 = 2\rho d\nu,$$

since the quantities $\mathbf{d}$ are vector amplitudes.

Further,

$$\int_{-\infty}^{+\infty} \left(\frac{\sin^2 x}{x^2} + \left(\frac{\sin x}{x^2} - \frac{\cos x}{x} \right)^2 \right) dx = \frac{4\pi}{3}.$$

Replacing the summation by integration, and performing one of the two integrations (remembering that the result must be divided by 2 if in the first integration the limits of $N_1 - N_2$ are taken as $-\infty$ and $+\infty$ because each combination term we agreed to count only once in the summation),

$$\bar{\epsilon}^2 = \frac{4\pi r^3}{3} \int_0^\infty \frac{c^3}{8\pi} \frac{\rho^2}{\nu^2} d\nu. \quad . \quad . \quad . \quad (6')$$

To a first approximation in the complex notation

$$\dot{x} = ed_x/(2\pi i\nu m), \quad \text{where } i = \sqrt{-1}.$$

We must consider the value of X given by

$$X = \frac{e^2}{2\pi m\nu c} \sum \int_t^{t+\tau} \left\{ [\mathbf{d}_1, \mathbf{h}_2]_x \cos \left(2\pi\nu_1 t - 2\pi\psi_1 - \frac{\pi}{2} \right) \right. \\ \left. \times \cos 2\pi(\nu_2 t - \psi_2) \right. \\ \left. + [\mathbf{d}_2, \mathbf{h}_1]_x \cos 2\pi(\nu_1 t - \psi_1) \cos \left(2\pi\nu_2 t - 2\pi\psi_2 - \frac{\pi}{2} \right) \right\} dt.$$

Squaring, averaging, and neglecting terms in $(\nu_1 + \nu_2)^{-1}$, as well as higher-order terms in $\nu_1 - \nu_2$, in the usual manner,

$$2 \left(\frac{4\pi mc}{e^2} \right)^2 \frac{\bar{X}}{\tau} = \sum \frac{([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)^2}{\nu^2} \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2} \\ + 2 \sum_{\nu_1 - \nu_2 = \nu_3 - \nu_4} \frac{([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)([\mathbf{d}_3, \mathbf{h}_4]_x - [\mathbf{d}_4, \mathbf{h}_3]_x)}{\nu_1 \nu_3} \\ \times \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2} \cos 2\pi(\psi_1 - \psi_2 - \psi_3 + \psi_4)$$

where the first summation is extended over all combinations of indices (1) (2), each combination being counted once. In the second summation each term of the first summation is combined once with every other term. The first summation gives rise to the term taken into account by Fokker. In fact, the space average of $([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)^2$ is readily found to be $\frac{4}{9}(d^2)^2$.

Remembering that

$$\sum_{d\nu} d^2 = 2\rho d\nu,$$

and that

$$\int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx = \pi,$$

it is found that the contribution of the first summation is

$$(X^2/\tau)^1 = \frac{2}{9} \left(\frac{e^2}{4\pi mc} \right)^2 \int_0^\infty \frac{\rho^2}{\nu^2} d\nu. \quad \dots \quad (7')$$

Comparing the structure of formulæ (6) and (7), we see that the *phase terms*, *i. e.* terms depending on $\psi_1 - \psi_2 - \psi_3 + \psi_4$, are likely to contribute relatively as much to $\bar{\epsilon}^2$ and $\bar{X}^2/\tau$ in comparison with the absolute terms (6'), (7') if there is a grouping of waves so far as their direction of propagation is concerned.

We must remember here that the second term in (6) is extended over all such ν 's that $\nu_1 - \nu_2 = \nu_3 - \nu_4$, and also such that $\nu_1 - \nu_3 = \nu_2 - \nu_4$. This means that contributions to the sum will be brought about not only by having (1, 2) and (3, 4) in the same groups, but also by having (1, 3), (2, 4) in the same groups; for with this condition $\mathbf{d}_1\mathbf{d}_2 + \mathbf{h}_1\mathbf{h}_2$ is of the same sign as $\mathbf{d}_3\mathbf{d}_4 + \mathbf{h}_3\mathbf{h}_4$ if polarization persists through each group. There is a very much greater number of possibilities of such combinations than of the groupings (1, 2) (3, 4), and we are thus tempted to consider these as the only essential groupings. From this point of view, the average value of

$$(\mathbf{d}_1\mathbf{d}_2 + \mathbf{h}_1\mathbf{h}_2)(\mathbf{d}_3\mathbf{d}_4 + \mathbf{h}_3\mathbf{h}_4) \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right) \left(\frac{\sin x_{34}}{x_{34}^3} - \frac{\cos x_{34}}{x_{34}^2} \right)$$

is the same as that of

$$(\mathbf{d}_1\mathbf{d}_2 + \mathbf{h}_1\mathbf{h}_2) \left(\frac{\sin x_{12}}{x_{12}^3} - \frac{\cos x_{12}}{x_{12}^2} \right)^2.$$

Quite similarly in (7) the average value of

$$([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)([\mathbf{d}_3, \mathbf{h}_4]_x - [\mathbf{d}_4, \mathbf{h}_3]_x) \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2}$$

is the same as that of

$$([\mathbf{d}_1, \mathbf{h}_2]_x - [\mathbf{d}_2, \mathbf{h}_1]_x)^2 \frac{\sin^2 2\pi(\nu_1 - \nu_2)\tau}{\tau(2\pi(\nu_1 - \nu_2))^2}.$$

It is thus seen that the ratios in which (6), (7) are changed by the presence of the second terms may be the same.

§ 4. We shall consider now the relation of the problem of the motion of a free electron in black body radiation to that of the motion of a Bohr atom in the same radiation as considered by Einstein* in 1917. We must first of all decide in how far a free electron may be considered to be the limiting case of an electron bound to a Bohr atom. Let the binding to the nucleus be quasi-elastic, so that the equation of motion is

$$m\ddot{x} - \frac{e^2}{6\pi c^3} \ddot{x} + m\omega_0^2 x = e \left\{ d_x + \frac{1}{c} [\mathbf{v}, \mathbf{h}]_x \right\}.$$

Let us suppose temporarily that the term $\frac{1}{c} [\mathbf{v}, \mathbf{h}]_x$ has a negligible effect. Let d_x be periodic and of frequency $\frac{\omega}{2\pi}$. Then the amplitude $|x|$ of the vibration set up in x is

* Einstein, *Phys. Zeit.* xviii. p. 121 (1917).

related to the amplitude $|d_x|$ of $\dot{d}_x$ by

$$|x|^2 = \frac{e |d_x|^2}{m^2(\omega_0^2 - \omega^2)^2 + \left(\frac{e^2}{6\pi c^3}\right)^2 \omega^6} \quad (8)$$

If ω is near to the resonant value ω_0 , the ratio of the second term in the denominator to the first is that of $\frac{\omega^4 \left(\frac{e^2}{6\pi c^3}\right)^2}{4m^2(\omega_0^2 - \omega^2)^2}$ to $(\omega_0 - \omega)^2$. The width of the band to which the oscillator responds is therefore proportional to ω^4 , and is smaller for longer wave-lengths. Resonance for loosely-bound electrons is sharper than that of firmly-made Bohr atoms. We have therefore less reason for disregarding the effect of values of ω close to ω_0 in the case of loosely-bound electrons than we have in Einstein's case of 1917, and similarly we see more reason for taking into account values of $\omega \neq \omega_0$ in the case of firmly-built atoms than in Fokker's case.

The kinetic energy of a bound electron obtained from (8) and summed for all values of ω is in absolute value

$$\frac{m}{2} |\dot{x}|^2 = \frac{m}{2} \int_0^\infty \frac{\omega^2 e^2 |d_x^2|_\omega d\omega}{m^2(\omega_0^2 - \omega^2)^2 + \left(\frac{e^2}{6\pi c^3}\right)^2 \omega^6},$$

where the effective value of d_x^2 is taken.

The effect of frequencies in the neighbourhood of ω_0 is

$$\frac{m}{2} \int_0^\infty \frac{e^2 |d_x^2|_\omega d\omega}{4m^2 \left\{ (\omega_0 - \omega)^2 + \frac{\omega^4}{4m^2} \left(\frac{e^2}{6\pi c^3}\right)^2 \right\}} = \frac{3\pi^2 c^3}{2} \frac{|d_x^2|_{\omega_0}}{\omega_0^2},$$

where $|d_x^2|_{\omega_0}$ is the sum of the effective squares of all the $\dot{d}_x$ in a range $\omega - \omega_0 = 1$. Relatively to the energy present the kinetic energy attained due to resonance is thus seen to be greater for small values of ω_0 . (The Rayleigh-Jeans formula is, in fact, adjusted so as to make $|d_x^2|_{\omega_0}/\omega_0^2 = \text{const.}$) Thus again we see no definite reason for treating loosely-bound electrons on a basis different from rigidly bound atoms, and even expect loosely-bound structures to accentuate properties of resonance on account of a lower frequency and a decreased loss of energy by radiation.

Since a strictly free electron is a physical impossibility, we could put the whole problem on the basis of Einstein's which we have already discussed*. This, however, would

* G. Breit, Phys. Rev. Oct. 1923, pp. 313-319.

be unfair, because Einstein's problem of (1917) must be solved by taking into account other frequencies than those in the immediate neighbourhood of the emission line. This is indicated by the fact that matter has a refractive index for wave-lengths different from the emission wave-lengths, as well as by the possibility of thinking consistently of the motion of free electrons in which other frequencies than the natural $\nu=0$ are taken into account.

As shown in § 2, the vibratory motion is very small, and from §§ 2, 3 it follows that the contribution to $\bar{X}^2/\tau$ of the radiation pressure-effects becomes very small when $\nu \approx 0$. Thus free electrons may be thought of as the limiting case of bound electrons, the influence of frequencies outside the resonance band being in this case the more important. This can be shown to be the case by considering the radiation pressure-effects in the band and outside of it, the contribution in the band being found to vanish for infinitely loose binding on account of a small value of $\rho(\nu)$ for small ν .

It will be worth while to go into Einstein's case in slightly greater detail. Two states of the atom are considered: one of high energy ϵ_2 , and another of low energy ϵ_1 . A fall from ϵ_2 to ϵ_1 gives rise to the emission of $h\nu = \epsilon_2 - \epsilon_1$. A rise from ϵ_1 to ϵ_2 gives rise to the absorption of the same quantum. The spontaneous probability of emission in the time dt is $a dt$, the probabilities of absorption and of emission due to radiation are $b_1^2 \rho dt$ and $b_2' \rho dt$ respectively. The *a priori* probabilities of 1, 2 are p_1, p_2 respectively. For equilibrium

$$(a + b_1 \rho) p_2 e^{-\epsilon_2/kT} = b_1^2 \rho p_1 e^{-\epsilon_1/kT},$$

which leads to

$$\rho = \frac{a\nu^3}{e^{h\nu/kT} - 1},$$

where

$$a\nu^3 = \frac{a}{b_2^2}, \quad b_1^2 p_1 = b_2' p_2.$$

In order that the Brownian movement should give a kinetic energy of $kT/2$ per degree of freedom, Einstein's equation

$$\frac{\Delta^2}{\tau} = 2RkT \quad . \quad . \quad . \quad . \quad . \quad (9)$$

must be satisfied. Here Δ is the momentum imparted to the atom in the time τ , and Rv is the systematic resisting force to an atom having the velocity v . The term a gives rise to transitions which in the quantum theory correspond

to the dissipated energy of the classical case. It is for this reason that the correspondence principle relates α to the time constant of the classical theory. The amount of energy dissipated per second is then $p_2 e^{-\frac{\epsilon_2}{kT}} \alpha h\nu$. If the atom moves with velocity v , the amount of momentum absorbed from the radiation is $\frac{v'}{c^2}$ times this energy where

$$v' = v \left(3 - \frac{\nu}{\rho} \frac{\partial \rho}{\partial \nu} \right).$$

(See writer, *l. c.* Postulate 1.) Thus

$$R = \left(3 - \frac{\nu}{\rho} \frac{\partial \rho}{\partial \nu} \right) p_2 e^{-\frac{\epsilon_2}{kT}} \alpha \frac{h\nu}{c^2}. \quad . \quad . \quad . \quad (10)$$

Again, the average square of the fluctuation of energy is obtained by multiplying the number of transitions between

(1), (2) by $h^2 \nu^2$. This is per second $2p_1 e^{-\frac{\epsilon_1}{kT}} b_1^2 \rho (h\nu)^2$. If it is granted that this result must be divided by c^2 in order to obtain $\bar{\Delta}^2/\tau$ [See writer, *l. c.* Postulate 2. This condition is an expression of the statistical equivalence of $\mathbf{d}$ and $\mathbf{h}$ and

of the physical existence of the force $\frac{e}{c} [\mathbf{v}, \mathbf{h}]$ alongside with $e\mathbf{d}$], we have then

$$\frac{\bar{\Delta}^2}{\tau} = 2p_1 b_1^2 e^{-\frac{\epsilon_1}{kT}} \rho \left(\frac{h\nu}{c} \right)^2. \quad . \quad . \quad . \quad . \quad (11)$$

Substituting (10), (11) into (9), it is found that (9) is satisfied if

$$\rho = \frac{\alpha \nu^3}{e^{h\nu/kT} - 1}.$$

The writer's postulates (1), (2) are thus sufficient conditions in order that (9) should be satisfied. Postulate (1) is identical with the supposition we have made in § 2 above as to the nature of Fokker's Q. Postulate (2) is less specific than the treatment of Fokker's $\bar{X}^2/\tau$ in §§ 2, 3. But both involve the same idea: viz., the agitating influence is the

force $\frac{e}{c} [\mathbf{v}, \mathbf{h}]$ which acts simultaneously with the force $e\mathbf{d}$.

In the case of free electrons the transitions in the motion are gradual, and the calculation of both the absorbed energy and

the absorbed momentum is manageable by the classical theory. In the case of a quantized atom the motion changes discontinuously. When the motion changes from the state (1) to the state (2), we assign a greater energy to the atom. Our postulate (2) has then the meaning that if the absorption of energy should be pictured as work done on a resonator, and if simultaneously the amount of transferred momentum due to $\frac{e}{c}[\mathbf{v}, \mathbf{h}]$ should be computed, then this momentum may be assigned to the atom simultaneously with the assignment of the absorbed energy. This momentum is not necessarily $\frac{h\nu}{c}$. The statistical effect of this momentum is, however, the same as that of Einstein's needle quanta. So far both problems may be thought of in terms of the force equation

$$\mathbf{F} = \mathbf{d} + \frac{1}{c}[\mathbf{v}, \mathbf{h}],$$

where it is remembered that a certain amount of work must be done by the force before the atom changes from 1 to 2.

§ 5. One of the fundamental objections to classical electrodynamics is its apparent inability to explain the large accumulation of energy which is necessary for the absorption of a quantum in experiments on the photoelectric effect. The amount of energy carried by a plane wave across an area of atomic dimensions is calculated, and is found to be too small to give a quantum in a reasonable length of time*. It does not seem to the writer that a calculation of this sort is capable of deciding what the absorbed energy may be. In fact, on the classical theory the quantity which is spoken of as absorbed energy is *force times distance*

where the force is $e\mathbf{d} + \frac{e}{c}[\mathbf{v}, \mathbf{h}]$, and the distance is the distance travelled by the charge on which the force is exerted. The theorem of conservation of energy on classical electrodynamics is devised in such a way as to account for the absorbed energy by means of quantities connected with the field. It states that the energy absorbed by matter is absorbed at the expense of the energy stored in space (or æther) and the flux of Poynting's vector into the space. The energy flowing across a section of a plane wave in the absence of an

* Millikan, 'The Electron,' p. 232 (Univ. of Chicago Press, 1916). See also reference to Lord Rayleigh's criticism, *Phil. Mag.* xxxii. p. 188 (1916).

atom has thus little to do with the amount of energy which may be absorbed by an atom when placed into the wave.

On the classical theory, a charge the motion of which is confined to a small region may absorb from a plane wave an amount of energy which is great in comparison with the energy flowing over the region due to the wave in the absence of the charge. All that is necessary for this is a properly controlled vigorous motion of the charge which keeps its velocity in phase with and parallel to the electric vector of the wave. Inside a surface just enclosing the region to which the charge is confined there is not enough field energy to supply the demand of the theorem of conservation, but this amount is automatically satisfied by the flux of Poynting's vector through the surface. The essential addition to the field of the wave is the magnetic field due to the moving charge. This gives rise to a term in Poynting's vector which, when integrated over the surface, gives a flux contributing the main part of the necessary energy.

We must next decide what element in the atom and what characteristics of its motion we should consider in order to compute the energy absorbed. Bohr's principle of correspondence is of fundamental importance in this connexion, for it indicates the manner in which the classical radiation

force $\frac{e^2}{6\pi c^3} \ddot{v}$ finds expression in the quantum theory. This radiation force is neglected in the formulation of quantum conditions. However, the sin committed by forgetting it is punished by the failure of the atom to conform to quantum rules rigidly. The atom has a spontaneous tendency, given by Einstein's A_m^n (our symbol a of the preceding §), to fall from a high energy state to a low one; and this tendency is such that on the average the emission of energy from a set of atoms put into Einstein's state n may be likened so far as the frequency and the intensity of the radiation are concerned to the radiation from a set of "corresponding" classical mechanisms, these being essentially constant frequency vibrators having in their motion a close similarity to the mean motion of the electron between the two states m, n . So far as frequency is concerned, the analogy is exact (Bohr's correspondence theorem). So far as intensities go, the analogy or another similar analogy is probably exact also (Bohr's correspondence principle). Now, the amount of energy radiated may be thought of as the amount of energy dissipated in the motion of the atom owing to the action of

the radiation force $\frac{e^2}{6\pi c^3} \ddot{v}$. This force may be thus thought

of as exerting a cumulative effect on the equivalent corresponding resonator. When the accumulated dissipated energy acquires the value $h\nu$, the atom jumps from m to n .

The force $\frac{e^3}{6\pi c^3} \ddot{v}$ is a stranger to the quantum conditions.

It affects them only inasmuch as it makes strictly periodic motions impossible, except in quantum orbits of lowest energy, and the width of spectral lines may be thought of by formal quantum theory when violations in the simple periodicity due to the quantum jumps are considered*. Similarly, the force due to the exciting wave is a stranger to quantum conditions, and its action is similarly cumulative. The wave can be thus thought of as doing work on the "corresponding vibrator." If the frequency of the wave is equal to the frequency of the vibrator (neglecting the

broadening of that frequency due to the action of $\frac{e^2}{6\pi c^3} \ddot{v}$),

work will be done at a steady rate, and ultimately a quantum $h\nu$ will be absorbed. Then the atom leaves the state n and goes into the state m . Similarly, while it is in the state of high energy m , the phase of the wave may turn out to be such that the wave does a negative amount of work

($= -h\nu$) on the atom (or perhaps this, together with $\frac{e^2}{6\pi c^3} \ddot{v}$,

does that work). As a result, a jump from n to m takes place. It is seen, therefore, that a fairly concrete explanation of the correspondence principle and of the position of absorption bands of a substance may be obtained by the introduction of the *corresponding vibrators* together with a consideration of

the effects of $\frac{e^2}{6\pi c^3} \ddot{v}$. The quantitative side of the absolute

coefficients of absorption has been discussed by Ladenburg and Reiche, and by Milne †. Their discussions, however, are based on a formal appeal to the principle of correspondence and do not depend on the mechanism just proposed.

In calculation of the photoelectric effect, our picture can be used only if there is sufficient possibility for the absorption of a quantum. The amount of energy absorbed per unit time

* G. Breit, Proc. Nat. Acad. ix. no. 7, pp. 244-246 (July 1923).

Added in proof. For similar considerations, see Tolman, Phys. Rev. p. 693, June 1924. Ehrenfest and Tolman, Phys. Rev. p. 287, Sept. 1924.

† Ladenburg and Reiche, *Naturwissenschaften*, xi, p. 584 (July 1923). Milne, Phil. Mag. xlvii. p. 209 (1924). Ladenburg, *Zeitsch. f. Phys.* iv. p. 451 (1921).

from a wave having an electric intensity of amplitude d , a frequency ν , and in exact synchronism with the vibrator, is then $\pi e d A \nu$, where A is the amplitude of the vibrator. This amplitude we relate to the amplitude of the electronic motions, and we suppose that it is the same as the amplitude which must be considered for emission. For our present purpose we need to know only the order of magnitude of the amplitude, and we may take it to be the radius of the electronic orbit. The value of d involves some uncertainty. Let us suppose that we are dealing with a monochromatic wave emitted by a flame sending out N quanta per second. If we should calculate on the old viewpoint the amount of energy flowing per second through an area of atomic dimensions at a distance of r cm. from the source that energy would be $\frac{N h \nu}{4 \pi r^2} \pi a^2$, where a is the atomic radius. The number of quanta sent through per second is then $N a^2 / (4 r^2)$. With

$$N = 10^{14}, \quad a = 10^{-8} \text{ cm.}, \quad r = 100 \text{ cm.},$$

this is 2.5×10^{-7} . Thus one must wait 4×10^6 sec. before a quantum is absorbed on the view that Poynting's flux of the original plane wave accounts for the absorption. A quite different result is obtained if we adopt the view of work done on the equivalent resonator.

Let the time of emission of each quantum be τ (length of wave train $= c\tau$). Using electrostatic units and letting

$$d = E_0 \cos \omega t,$$

the value of E_0 is determined by

$$4 \pi r^2 \frac{1}{8 \pi} E_0^2 c \tau = h \nu.$$

During the interval τ there are $N\tau$ wave trains emitted. Provisionally we may assume that the phases of these are random. The resultant value of E_0^2 is then given by

$$E_0^2 = \frac{2N}{r^2} \frac{h \nu}{c}.$$

The number of quanta absorbed which could be absorbed per second if the absorption should go on at the maximum rate is then

$$ae \frac{\pi \nu}{h \nu} \sqrt{\frac{2N h \nu}{r^2 c}} = \frac{\pi a e}{r} \sqrt{\frac{2N \nu}{ch}},$$

with

$$a = 10^{-8} \text{ cm.}, \quad r = 10^2 \text{ cm.}, \quad N = 10^{14}, \quad \nu = 10^{15} / \text{sec.};$$

this gives 5×10^3 . Thus an atom must wait only 0.0002 sec.

before a sufficient amount of work has been done. Between the old view and the one here presented we see thus a divergence by a factor 2×10^{10} *.

Even though the view presented here is numerically very much more satisfactory than that previously held, the estimate of time which we just made is likely to be too high. One reason for this is the possibility of interference actions in the wave front such as has been suggested by Lorentz. The other is the purely theoretical possibility of cumulative actions due to previous influence on the atom. For we are computing essentially the storing of energy due to work done on the equivalent oscillator, and we must admit the possibility of this storing being cumulative in the sense that atoms which have been exposed previously and which have stored some energy need a smaller additional amount. From this point of view our calculation applies to fresh atoms only.

Even though we attempt above to look at absorption as related to the classical absorption, we do not wish to imply that the phenomenon is a classical one. All experimental evidence points to the opposite conclusion, viz. that there are transitions between discrete states. The probability of these transitions, however, is calculable on a classical basis, as pointed out above. This view is similar to that of Mie †. It is an extension of the principle of correspondence to the case of absorption, provided the principle of correspondence is formulated in terms of the force $\frac{2e^2}{3c^3} \ddot{v}$.

The exact manner in which external influences are to be considered as acting on the equivalent resonator is, of course, uncertain. That some such action exists, however, appears to be indicated by various phenomena. Anomalous dispersion apparently has no other possible explanation than that of an interaction between the incident wave and the equivalent resonator. It is of interest to observe in this connexion that as long as the frequency ν of the incident wave is different from the frequency ν_0 of the equivalent oscillator (supposed here for simplicity infinitely sharp), there is no experimental indication of a true change in the quantum

* The order of magnitude of Lord Rayleigh's correction is 10^6 . The γ -ray difficulty cited by Millikan is not necessarily real, because the electrons absorbing γ -rays may be much more rapidly moving than the optical ones.

† G. Mie, *Ann. der Physik*, lxxiii. p. 195 (1924).

state of the atom. This may be interpreted in two ways: (a) the work done on the equivalent resonator by the incident wave is never comparable to $h\nu$ if $\nu - \nu_0 \neq 0$; (b) the transitions between levels the energy difference of which is given by $\Delta W = h\nu_0$ cannot be caused by values of $\nu \neq \nu_0$ (disregarding, for the present, diffuseness of quantization). Which of these hypotheses is true is very hard to answer. However, it appears that (a) is likely to be the case. In fact, let the motion of the oscillator be given by

$$x = A \sin 2\pi\nu_0 t,$$

and let the x component of the electric intensity of the incident wave be $E_0 \cos(2\pi\nu t - \psi)$. The amount of work done by the wave between the instants t_1, t_2 is then

$$\frac{1}{2} E_0 e \nu_0 A \left[\frac{\sin(2\pi(\nu - \nu_0)t - \psi)}{\nu - \nu_0} + \frac{\sin(2\pi(\nu + \nu_0)t - \psi)}{\nu + \nu_0} \right]_{t_1}^{t_2}.$$

Only the first term in this expression is of importance. The maximum value of absorbed energy due to it is $\frac{E_0 e \nu_0 A}{2(\nu - \nu_0)}$.

In order that this term should be appreciable in comparison with the action of a wave for which $\nu = \nu_0$ acting for a time τ , we must have $\frac{1}{\nu - \nu_0}$ comparable to τ . For the time τ we

may take the time corresponding to the length of a wave train, and thus corresponding according to the measurements of Wien* and numerous other evidences to the time constant on the classical theory. We shall show presently, however,

that $\frac{1}{\nu - \nu_0}$ is comparable to τ only if the frequency ν is within the width of the emission line ν_0 . We see, therefore, that as long as resonance is sharp, we need not be concerned with a differentiation of the possibilities (a), (b).

The property of $\frac{1}{\nu - \nu_0}$ in relation to τ which we have just used is related to some general properties of oscillators which are conveniently kept in mind in connexion with the subject here discussed. These properties are expressed by

* W. Wien, *Ann. der Physik*, lxxiii. p. 483 (1924).

the mathematical identities

$$2\tau_0\tau_1 \int_{-\infty}^{+\infty} \frac{d\nu}{[1 + (2\pi(\nu - \nu_0)\tau_0)^2][1 + (2\pi(\nu - \nu_1)\tau_1)^2]} \\ = \frac{\frac{\tau_0\tau_1}{\tau_0 + \tau_1}}{1 + \left(2\pi(\nu_1 - \nu_0) \frac{\tau_0\tau_1}{\tau_0 + \tau_1}\right)^2}, \quad (\text{I.})$$

$$\int_{-\infty}^{+\infty} \frac{\cos(2\pi\nu t)}{1 + (2\pi(\nu - \nu_0)\tau)^2} d\nu = \frac{e^{-|t|/\tau}}{2\tau} \cos(2\pi\nu_0 t), \quad (\text{II.})$$

$$\int_{-\infty}^{+\infty} \frac{(2\pi(\nu - \nu_0)\tau) \sin(2\pi\nu t)}{1 + (2\pi(\nu - \nu_0)\tau)^2} d\nu \\ = \frac{e^{-|t|/\tau}}{2\tau} \frac{|t|}{t} \cos(2\pi\nu_0 t). \quad (\text{III.})$$

Formulas (II.), (III.) show that a damped wave beginning at $t=0$ and having the time constant τ (represented by $\frac{1}{2\tau} e^{-|t|/\tau} (1 + |t|/t) \cos(2\pi\nu_0 t)$) may be thought of as the sum of the two Fourier integrals on the left-hand sides of (II.), (III.). Adding (II.), (III.), we have

$$\int_{-\infty}^{+\infty} \frac{\cos(2\pi\nu t - \tan^{-1})(2\pi(\nu - \nu_0)\tau)}{\sqrt{1 + (2\pi(\nu - \nu_0)\tau)^2}} d\nu \\ = \frac{e^{-|t|/\tau}}{2\tau} (1 + |t|/t) \cos(2\pi\nu_0 t). \quad (\text{IV.})$$

The main contributions to the integral on the left come from a band of frequencies determined by such values of ν that $2\pi(\nu - \nu_0)\tau$ is not too great in comparison with unity. This shows that the band of frequencies which would be emitted by an oscillator would be confined to a region in which the time $\frac{1}{\nu - \nu_0}$ is not too small in comparison with τ .

Again, the motion of the oscillator is given by

$$\ddot{x} + \kappa\dot{x} + (2\pi\nu_0)^2 x = \frac{F_{l,x} e}{m}, \quad (\text{V.})$$

where ν_0 is the natural frequency, κ the dissipation factor

given by $\kappa = \frac{2}{3} \frac{e^2}{c^2} (2\pi\nu)^2$ on the electrostatic system of units. The time constant $\tau = \frac{2}{\kappa}$. If E_x is of the form $E_x \cos(2\pi\nu t - \psi)$, the absolute value of the forced vibration in x is given by

$$x = \frac{E_x \cdot e \cdot m}{\sqrt{(2\pi\kappa\nu)^2 + (2\pi)^2(\nu_0^2 - \nu^2)^2}} \dots (VI.)$$

It is easily seen that the expression under the radical of this formula is very nearly $(2\pi\kappa\nu)^2 [1 + (2\pi\nu - \nu_0\tau)^2]$. Thus forced vibrations have an appreciable value only if the time $\frac{1}{\nu - \nu_0}$ is not too great in comparison with the time constant τ^* .

Further, according to equation (I.) the effect of a damped wave (IV.) having the time constant τ , and a natural frequency ν on a resonator having a time constant τ_1 and a natural frequency ν_1 depends on $\nu_1 - \nu$ in such a way as though the resonator were undamped and the wave had a small time constant

$$\left(\frac{1}{\tau_0} + \frac{1}{\tau_1}\right)^{-1} = \frac{\tau\tau_1}{\tau_0 + \tau_1},$$

or otherwise in such a way as though the wave were undamped and the resonator had a time constant $\frac{\tau\tau_1}{\tau_0 + \tau_1}$. (The Bjerknes decrement law †.)

* It is of interest to note that to within the approximation here considered, the amplitude induced in a resonator by a wave of frequency ν and given by (VI.) is proportional to the amplitude of the component oscillation in the Fourier integral (IV.). This means that the width and the spectral distribution of the band of frequencies from which the resonator absorbs energy is the same as the width of the bands into which it radiates. If it were not for this fact there could be no true equilibrium of a resonator with black body radiation.

† From (I.) we obtain the following results:—

(a) We have:

$$\begin{aligned} 2\tau_0^{-1}\tau_1^{-1} \int_{-\infty}^{+\infty} \frac{d\nu}{[1 + 2\pi(\nu - \nu_0)\tau_0^{-1}]^2 [1 + (2\pi(\nu - \nu_0)\tau_1^{-1})^2]} \\ = 2(\tau_0 + \tau_1) \frac{\left(\frac{\tau\tau_1}{\tau_0 + \tau_1}\right)^2}{1 + \left(2\pi(\nu_0 - \nu_1)\frac{\tau\tau_1}{\tau_0 + \tau_1}\right)^2} \end{aligned}$$

This we interpret by saying that an oscillator having a time constant τ_1 when subjected to a group of damped wave trains recurring periodically at intervals of 1 second having a peak amplitude 2 and a time constant τ (see (IV.)), acquires an average energy which is $2\tau_0 + \tau_1$ times the

These resonance relations, which are of importance in wireless telegraphy, are known to be true experimentally, and it is natural to require an extension of these relations in the quantum theory of spectral lines. Equation (IV.) appears to be the natural viewpoint to take in the quantum

energy which would be acquired by a resonator having the same mass and restitution constant, but a decreased time constant $\tau' = \frac{\tau_0 \tau_1}{\tau_0 + \tau_1}$ if this resonator were exposed to a monochromatic wave of frequency ν_0 and of unit amplitude.

(b) We have:

$$(2\tau_0)^2 \tau_1 \int_{-\infty}^{+\infty} \frac{d\nu}{[1 + (2\pi(\nu - \nu_0)\tau_0)^2][1 + (2\pi(\nu - \nu_1)\tau_1)^2]} \\ = 2\tau_0 \frac{\frac{\tau_0 \tau_1}{\tau_0 + \tau_1}}{1 + \left(2\pi(\nu_1 - \nu_0) \frac{\tau_0 \tau_1}{\tau_0 + \tau_1}\right)^2}.$$

This means that the energy dissipated by an oscillator having a time constant τ_1 from a group of waves having a time constant τ_0 , recurring periodically at intervals of 1 sec. and having a peak amplitude 2, is $2\tau_0$ times the energy which would be dissipated by an oscillator having a time constant $\frac{\tau_0 \tau_1}{\tau_0 + \tau_1}$ (with mass and restitution constants unchanged).

from a monochromatic wave of frequency ν_1 and unit amplitude.

The right-hand side of the above equation may be re-written as

$$\frac{1}{2} \frac{\tau_0 + \tau_1}{\tau_1} \frac{\left(\frac{2\tau_0 \tau_1}{\tau_0 + \tau_1}\right)^2}{1 + \left(2\pi(\nu_1 - \nu_0) \frac{\tau_0 \tau_1}{\tau_0 + \tau_1}\right)^2}.$$

Since

$$\int_{-\infty}^{+\infty} \frac{\tau_2 d\nu}{1 + (2\pi(\nu - \nu_1)\tau_2)^2} = \frac{1}{2},$$

we can state that the energy dissipated may be also thought of as that dissipated from a group of damped waves with a time constant $\frac{\tau_0 \tau_1}{\tau_0 + \tau_1}$ having unit group frequency, a peak amplitude of 2, a frequency ν_0 , and acting on a very sharp resonator with a very large time constant τ_2 , provided that energy is multiplied by $\frac{(\tau_0 + \tau_1)}{\tau_1}$.

As special cases from (b) we obtain

(b') The energy dissipated by an infinitely sharp resonator from a group of waves having a peak amplitude 2, a group frequency 1, and a time constant τ_0 is $2\tau_0$ times the energy dissipated from a monochromatic wave train of unit amplitude, of frequency ν_0 , by a resonator having a time constant τ_0 .

theory. A damped wave is resolved by this equation in a Fourier integral. The expansion happens to be of such a nature as to be similar to (VI.) integrated over ν . It appears natural to require the same similarity in the quantum case. Further, if the physical information of equation (I.) (the reciprocity of τ_0, τ_1) may be legitimately extended to the quantum case, then it appears that one must either form a dynamical model leading ultimately to spectral distributions equivalent to (IV.) or else one must postulate the direct applicability of (I.).

It is natural to look for a quantum-theory analogue of (I.), because the simplest fundamental phenomenon is the transition of one atom from a state of high energy to one of low followed by a transition of another atom in the reverse direction. The first phase leads to the emission of a quantum having a finite length of emission, and therefore the general characteristics of (IV.). The second phase is the absorption of that quantum. This we may suppose to happen in a manner analogous to (I.). If such is the case, we should expect that experiments on the absorption of resonance radiation will give apparently larger width of spectral lines than one should suppose from the value of τ . If the emitting and absorbing atoms have the same τ_0 , the effective value of τ is $\tau_0/2$.

The writer knows of no direct experimental evidence bearing on the existence of such effects. However, by analogy with classical theory it would be surprising if they were absent, and further it would be very difficult to see how equilibrium with black body radiation is maintained unless the emission and absorption bands have the same width and spectral distribution. The formulation of quantum theory does not seem satisfying therefore before one is able to account for the width of lines for emission as well as absorption on the same basis. A tentative theory explaining the width due to collisions on the same basis as the intrinsic width has been given by the writer (Proc. Nat. Acad. *l. c.*). A different and in all probability more correct point of view is taken by Bohr*, who ascribes the width of lines to an intrinsic inaccuracy in the applicability of quantum rules which causes the spectral width. Whether the broadening is actual as suggested by Bohr, or statistical as the above would suggest, the order of magnitude of the effect is such as would be caused on a classical resonator

* *Zeits. f. Phys.* xiii. pp. 145-153.

damped by the force $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$, or else undamped but interrupted by external influences at time intervals comparable with the time constant of the damped resonator*. Thus here also there is a certain similarity of the action of the $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$ and of the external forces. To summarize :

- (1) The equations of motion of an electron in its orbit are to a first approximation classical, provided the radiation force $\frac{2}{3} \frac{e^2}{c^3} \ddot{v}$ and the wave force $e\mathbf{d} + \frac{e}{c} [\mathbf{v}\mathbf{h}]$ are disregarded.
- (2) The electron leaves its quantized state and passes into a state of higher or lower energy if the amount of work done on it by either of the neglected forces is equal to the energy difference between these states (or perhaps both). The forces are regarded as acting on a collection of equivalent resonators which represent the mean motions of the electron between various quantized states.
- (3) Besides the function of determining probabilities of transitions between quantum states, each of the equivalent resonators of frequency ν_0 acts on incident wave of frequency ν as though it were a classical resonator. This view is forced on us by phenomena of dispersion†.

The writer's purpose in sketching the above theory is to point out that the classical wave theory, if given proper attention, is not powerless in dealing with phenomena for which light-quanta have been especially devised. He may be permitted to call attention to a phenomenon (in addition to those of interference and diffraction which are strongly

* The question as to a possible difference in the width of an emission and an absorption line, which has been discussed in the above-mentioned note, must apparently be answered in the sense that such a difference does not exist, for otherwise the equilibrium with black body radiation would not be maintained. This is true even in such radiation fields in which the atom rests in the lowest state a very long time before passing to an upper level.

† One can state this definitely only for frequency ν not too far from ν_0 . However, in a purely speculative manner one might suppose that the deviation of atomic dynamics from classical is due to an interaction between electrons taking place in terms of equivalent resonators rather than according to the inverse square law.

emphasized by Bohr) which apparently is in favour of classical wave theory. This is the tendency of a γ -ray to emit β -rays out of the atom in which the γ -ray is produced. The inapplicability of light-darts is mentioned by Meitner*. It is of interest to point out that on the wave theory, estimating the time of emission of the γ -rays by the classical formula, a value of the electric intensity in the neighbourhood of the K ring results which is comparable with the electrostatic field due to the nucleus. It seems very natural from the point of view of the wave theory that the electron is thrown out under these circumstances. The evidence from the Compton effect at the present time is not very decisive, especially on account of a possible classical Doppler effect which is pointed out by Bauer†. It will suffice to state that the original Compton effect was diffuse; that the tertiary radiation effect of Duane, Clark, and Stifler is also diffuse; but that the lines photographed by J. A. Becker, E. C. Watson, W. R. Smythe, R. B. Brode, and L. M. Mott-Smith are sharp‡.

After writing the article the writer received the May number of the 'Philosophical Magazine,' in which Bohr, Kramers, and Slater deal with the "virtual" resonators in connexion with optical phenomena in general. In many respects the views proposed here are similar to theirs. The aspects of the reactions discussed are different, however. The writer is very grateful to Prof. J. H. Van Vleck for many valuable comments.

The University of Minnesota,
June 3rd, 1924.

* L. Meitner, *Zeits. f. Phys.* xix. p. 307 (1923); C. D. Ellis, *ibid.* x. p. 203 (1922), and *Proc. Camb. Phil. Soc.* xxvi. p. 274 (1922); L. Meitner, *Zeits. f. Phys.* xi. p. 35 (1922).

† E. Bauer, *C. Rend.* clxxvii. pp. 1031-1033 (1923).

‡ American Physical Society, Washington Meeting, April 25-26.

Added in proof.—At the Washington Meeting of the American Physical Society (Dec. 1924) an apparently definite verdict in favour of the Compton effect has been obtained. As stated, however, this does not contradict the views presented.

LX. *The Mobility of the Positive Ions in Air.*

By H. B. WAHLIN*.

RECENT determinations of ionic mobilities have shown that the nature of the ions formed when a gas is ionized by α particles is more complex than was hitherto supposed to be the case. Erikson †, using a modification of the air-stream method for determining mobilities, has demonstrated the existence in air of positive ions having mobilities of 1.35 and 1.89 cm./sec./volt/cm. The higher value was obtained if the mobility was determined soon after the ions were formed, and the lower value if the ions were allowed to remain in the gas for about .5 sec. before the measurements were made. This lower mobility may be termed the normal mobility, since it represents the value for the most stable form of the ion after it has remained in the gas for an appreciable length of time. It is the value generally ascribed to the positive ion in air.

The most obvious explanation of Erikson's results is that the initial ion when aged picks up one or more neutral molecules to form a heavier ion, and therefore one with a lower mobility.

Nolan ‡, using the alternating field method as well as the air-stream method, has been able to obtain not only the values given above, but values much higher than those observed by Erikson. He found mobilities as high as 11.2 cm./sec./volt/cm. for the positive ion.

The work presented herewith was undertaken to determine if ions having mobilities lower than the value ascribed to the normal ion could exist in air. The method used was the Franck modification of the Rutherford alternating current method, and has been described in an earlier paper §. The ions were produced in an auxiliary chamber and were driven through a gauze by a field which could be varied from 2/10 volts/cm. to 39 volts/cm. The polonium used as an α particle source was so arranged that the ions had to pass through an appreciable layer of the unionized gas before passing through the gauze into the alternating field. Thus, by using a low auxiliary field, all the ions could be aged for a longer time than would be the case if the entire space in the auxiliary chamber were under the influence of the ionizing radiation. In this case an appreciable number of

* Communicated by the Author.

† Erikson, H. A., *Phys. Rev.* n. s. xx., Aug. 1922.‡ Nolan, J. J., *Proc. Irish Roy. Acad.* xxxvi. A (1923).§ Wahlín, H. B., *Phys. Rev.* Sept. 1922.

the unaged ions would pass into the alternating field even if the auxiliary field were so low as to allow the greater portion of the ions to become aged. The effect of such a condition would be to cause the mobility curves to approach the voltage axis less sharply, and consequently make a determination of the mobility from the intercept inaccurate.

The alternating field used in these determinations was obtained from the 60 cycle alternating current lighting circuit, and also from a vacuum-tube oscillator of the Hartley type. The frequency of this oscillator could be varied from 180 cycles/sec. to as high a value as was desired. When the oscillator was used, the alternating potential was obtained by grounding one side of the condenser in the oscillating circuit, and connecting the other side through the necessary key to the gauze. The alternating potential could then be varied by adjusting the plate voltage only.

Since the ions can age after passing through the gauze as well as before, it is necessary that the alternating field be as high as possible so that the ions will reach the collecting plate in a time short compared with the time necessary for ageing to take place. For this reason, the mobilities were determined in as high fields as could be measured accurately.

The air used in these determinations was dried by passing it slowly through a tube 75 cm. long filled with potassium hydroxide, then through a similar tube filled with calcium chloride, through two tubes of the same length containing phosphorus pentoxide, and finally through a trap cooled with liquid air, and a coil also immersed in liquid air. From this coil it passed into the measuring chamber. Water vapour as well as any other condensable vapours would thus be reduced to a minimum. The coil was in direct connexion with the chamber, and was therefore kept immersed in liquid air during a series of determinations.

Mobilities were determined with alternating fields ranging from 45 volts/cm. to 105 volts/cm., and with auxiliary fields as given above. The method of procedure was the usual one of measuring the charge received by the collecting plate in a given time for different values of the alternating potential. This charge can be taken as a measure of the current. From the data thus obtained a curve of the current against alternating voltages is plotted, and the mobility determined from this.

If only one type of ion were present, one would expect a smooth curve which would approach the voltage axis quite sharply. If more than one type of ion, each with a different mobility, were present, however, these curves would show

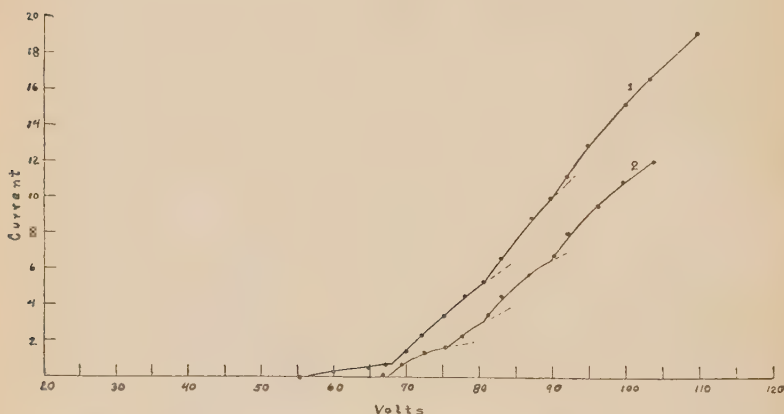
quite sharp breaks. The resultant curve would in this case consist of a number of mobility curves each with a definite voltage intercept superimposed on a curve with a lower intercept. Therefore, from the breaks in the mobility curves as well as from the intercepts the mobility K may be determined by the relation

$$K = \frac{\pi n d^2}{\sqrt{2V}} \frac{P}{760},$$

where d is the distance between gauze and collecting plate, n is the frequency, V is the effective value of the alternating voltage, and P is the pressure in mm.

Fig. 1 illustrates the types of curves obtained at a pressure of 200 mm. with a distance d equal to 15.5 mm., and with

Fig. 1.

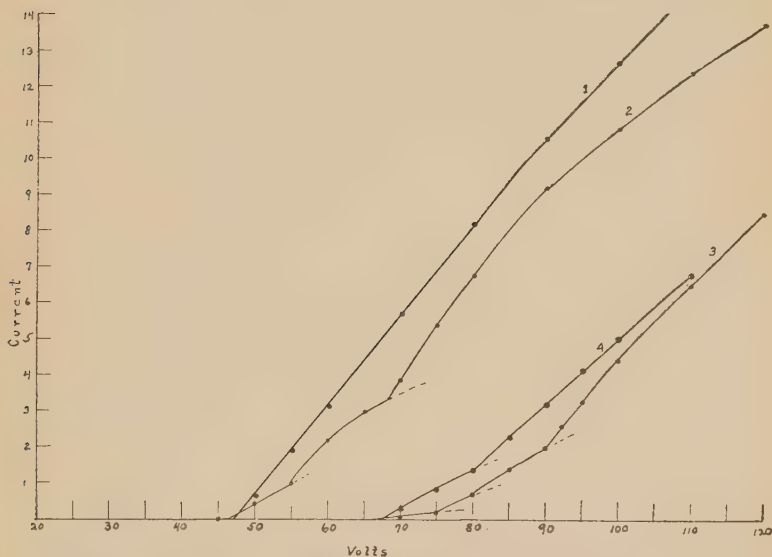


a frequency of 60 cycles/sec. Curve 1 was obtained with an auxiliary field of 3 volts/cm., and curve 2 with a field of 1.5 volts/cm. The curves shown in fig. 2 were obtained at a pressure of 50 mm. with a frequency of 230 cycles/sec., and with $d=15.5$ mm. Curve 1 was obtained with an auxiliary field of 37.5 volts/cm., curve 2 with a field of 18 volts/cm., curve 3 with a field of 25/100 volts/cm., and curve 4 with a field of 1.5. The breaks appearing between 65 and 68 volts give the normal mobility 1.35 cm./sec./volt/cm. Breaks above this would correspond to lower mobilities and those below this to higher mobilities.

As may be seen from an examination of these curves, with sufficiently low auxiliary fields, *i. e.*, when the ions have a long time in which to age, the ions become more complex. Curve 1, fig. 2, shows that the initial ion is of

one class only. It is possible that the initial ion observed here is a single molecule, and that the ageing consists in adding molecules or atoms to this. This, however, is not in accord with the work of Nolan, since he was able to observe ions with mobilities as high as 11.2 cm./sec./volt/cm., while the highest value observed in this work was 1.89 cm./sec./volt/cm. If this 1.89 ion corresponds to a single molecule ion, it would be difficult to account for the higher values obtained by Nolan. The writer was unable to observe the high mobilities given by Nolan. However, it is possible

Fig. 2.



that these age so rapidly that unless they are caught immediately after formation they will pass over into a less mobile type. If that is the case, the experimental conditions were not favourable for the observation of them.

In some cases there were indications of a break in curve 3, fig. 2, and curve 2, fig. 1, at about 105 volts. This break could not be repeated at will, however, so that the mobility computed from this point was not used.

The mobilities observed by the writer, together with the corresponding values found by Erikson and Nolan, are given below :—

Nolan		1.79	1.52	1.37			
Erikson		1.89	...	1.35			
Wahlin		1.89	1.57	1.35	1.20	1.10	.970

By an examination of the curves it may be seen that the 1.2 ion (intercept at 75 volts) disappears, as the ageing time is decreased, before the 1.10 ion. The explanation immediately suggests itself that this ion is due to a breaking down of the 1.10 ion. Possibly what happens is that the 1.35 ion adds on a molecule to form the 1.10 ion, and this loses an atom and forms the 1.2 ion.

The indications are therefore, that, while with average time of ageing the bulk of the ions present are such as to give a mobility of 1.35 cm./sec./volt/cm., with sufficient ageing ions with lower mobilities may be present. That the presence of these ions depends on the time of ageing is shown by the fact that the lower mobilities disappear as the ageing time is decreased, until finally those ions having a mobility of 1.89 cm./sec./volt/cm. predominate.

In conclusion the writer wishes to express his thanks to Mr. C. M. Bardin for his assistance in obtaining these data.

University of Wisconsin,
Madison, Wisconsin.

October 17, 1924.

LXI. *A Theorem in Tidal Dynamics.* By J. PROUDMAN
(*Tidal Institute, University of Liverpool*)*.

1. CERTAIN theorems on pairs of solutions of the wave-equation $(\nabla^2 + \kappa^2)\phi = 0$, of which Green's theorem is the root, are well known †. In the present paper ‡ these theorems are extended to the general dynamical equations of the tides.

Theorems of the type indicated appear likely to be helpful in the attempt to determine the characteristics of the actual tides far away from land. For example, if the tidal elevation is known at all points of the coast of a landlocked sea or ocean, the present methods provide a means of calculating the elevation at any point not on the coast. But the methods are not restricted to landlocked basins, as will be seen from §§ 5, 6.

The main theorem of the paper (§ 3) is a relation between certain integrals involving functions which satisfy the tidal equations, and also auxiliary functions which satisfy equations similar to, but not identical with, the tidal equations. The auxiliary functions contain a large arbitrary element and are not subject to any boundary conditions.

* Communicated by the Author.

† See for example, Lamb, 'Hydrodynamics,' Arts. 290, 305.

‡ Part of Adams Prize Essay, 1923.

Their determination is therefore free from the chief difficulty of tidal problems. For any distribution of ocean-depth they can be constructed by direct computational methods, and if the depth may be regarded as uniform they can be represented with great ease (§§ 5, 6).

2. General Equations of the Tides.

We shall denote by :

- a the radius of the Earth,
- Ω the angular speed of the Earth's rotation on its axis,
- g the acceleration due to gravity,
- θ, χ the co-latitude and east longitude of any point,
- x, y Cartesian coordinates in the mean surface of a flat sea,
- h the depth of water below any point of the mean surface,
- t the time,
- ζ the elevation of the free surface of the water at any time above any point of the mean surface,
- u, v, ν the mean values along any vertical of the velocity-components at any time in the horizontal directions of increasing θ, χ or x, y , and along the normal to a section respectively,
- $-g\bar{\zeta}$ the potential of the astronomical disturbing forces,
- F, G the components of the external frictional force per horizontal area and per density of the water,
- σ the speed of the harmonic tidal constituent considered.

It is convenient also to write

$$\omega = \Omega \cos \theta, \quad \zeta' = \zeta - \bar{\zeta}.$$

We shall consider a complex harmonic constituent, so that the time enters only through the factor $e^{i\sigma t}$ and only the real parts of the functions are to be interpreted.

The equation of continuity may be written as

$$\frac{1}{a \sin \theta} \left\{ \frac{\partial}{\partial \theta} (hu \sin \theta) + \frac{\partial}{\partial \chi} (hv) \right\} + i\bar{\sigma}\zeta = 0, \quad (2.1)$$

and the equations of motion as

$$i\sigma u - 2\omega v = -g \frac{\partial \zeta'}{a \partial \theta} - \frac{F}{h}, \quad i\sigma v + 2\omega u = -g \frac{\partial \zeta'}{a \sin \theta \partial \chi} - \frac{G}{h} \quad (2.2)$$

3. The Theorem.

We shall use a triad U, V, Z of auxiliary complex functions of θ, χ which are continuous and satisfy the differential equations

$$\frac{1}{a \sin \theta} \left\{ \frac{\partial}{\partial \theta} (hU \sin \theta) + \frac{\partial}{\partial \chi} (hV) \right\} + i\sigma Z = 0, \quad (3.1)$$

$$i\sigma U + 2\omega V = -g \frac{\partial Z}{a \partial \theta}, \quad i\sigma V - 2\omega U = -g \frac{\partial Z}{a \sin \theta \partial \chi}, \quad (3.2)$$

over the ocean. It is to be noticed that in defining these functions we have changed the sign of ω from (2.2).

Now take any definite region of the ocean and let N denote the component along the outward drawn normal at any point on its boundary of the vector whose components in the directions of θ, χ increasing are U, V respectively. By the aid of Green's Theorem applied to this region, we deduce from (3.1), (2.2)

$$\begin{aligned} \int h \xi' N ds &= \iint \frac{1}{a \sin \theta} \left\{ \frac{\partial}{\partial \theta} (h \xi' U \sin \theta) + \frac{\partial}{\partial \chi} (h \xi' V) \right\} dS \\ &= -i\sigma \iint \xi' Z dS + \iint h \left(U \frac{\partial \xi'}{a \partial \theta} + V \frac{\partial \xi'}{a \sin \theta \partial \chi} \right) dS \\ &= -i\sigma \iint \xi' Z dS - \frac{1}{g} \iint h \{ i\sigma (Uu + Vv) \\ &\quad - 2\omega (Uv - Vu) \} dS - \frac{1}{g} \iint (FU + GV) dS. \\ &\quad \quad \quad \dots \quad (3.31) \end{aligned}$$

Here the line-integrals are taken round the boundary of the region considered, and the surface-integrals are taken over its area. Similarly using (2.1), (3.2) we obtain

$$\begin{aligned} \int h Z v ds &= -i\sigma \iint Z \xi dS - \frac{1}{g} \iint h \{ i\sigma (uU + vV) \\ &\quad + 2\omega (uV - vU) \} dS, \quad \dots \quad (3.32) \end{aligned}$$

so that

$$\begin{aligned} \int h \xi' N ds - \int h Z v ds &= i\sigma \iint \xi Z dS - \frac{1}{g} \iint (FU + GV) dS. \\ &\quad \quad \quad \dots \quad (3.4) \end{aligned}$$

Equation (3.4) constitutes the theorem.

4. Corollaries.

Suppose that the functions U, V, Z are specially related to a particular point Q in such a way that for any point P on a circle of centre Q

$$2\pi \cdot QP \cdot hN \rightarrow \sigma l^3 \quad . \quad . \quad . \quad (4.1)$$

as $P \rightarrow Q$, where l is a convenient constant length. We shall say that the functions have a source at Q , at which point of course, on account of the infinity, they do not satisfy the condition of continuity laid down in § 3.

Let us suppose that U, V, Z are continuous at every point considered other than Q . Then on applying the

Fig. 1.



theorem of the last section to an annular region round Q (fig. 1), we obtain, on making the inner circuit shrink into Q ,

$$\sigma l^3 \zeta'_Q = \int h(\xi'N - Z\nu)ds - i\sigma \iint \xi Z dS, \quad . \quad . \quad (4.2)$$

on supposing that $F=G=0$. In (4.2) the line-integral relates to the outer curve only and the surface-integral to the whole area which it contains.

Equation (4.2) provides the means of calculating the elevation at any point inside a closed curve, providing we know the elevation and normal current all round the curve and frictional forces inside the curve may be neglected. In particular, we can calculate the elevation at any point inside a landlocked sea or ocean providing we know the coastal values. Once the functions U, V, Z have been constructed, the computations involved are of a direct and relatively simple kind.

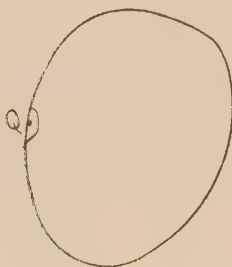
Next suppose that Q lies on the bounding curve of the region under consideration, but that for the purpose of

applying (3.4) we exclude Q by means of an arc of a circle having this point for its centre (fig. 2). We obtain, on making the circle shrink into Q ,

$$\frac{1}{2}\sigma l^3 \zeta'_Q - \int h \zeta' N ds = - \int h Z \nu ds - i\sigma \iint \zeta Z dS, \quad (4.3)$$

which is an integral equation of Fredholm's type, determining ζ' on the boundary when ν is known on the boundary. This

Fig. 2.



integral equation does not appear to have been previously given, though similar equations are familiar in the theory of potential. Integral equations which have been previously proposed for the solution of tidal problems involve Green's functions.

5. *Flat Sea of Uniform Depth.*

Now let us suppose that the region under consideration is small enough for the curvature of the Earth to be neglected, and also that we may take h as constant. The equations (3.1), (3.2) may be replaced by

$$\frac{\partial^2 Z}{\partial x^2} + \frac{\partial^2 Z}{\partial y^2} + \kappa^2 Z = 0, \quad \dots \dots (5.1)$$

$$\left. \begin{aligned} \frac{\sigma^2 - 4\omega^2}{g\sigma} U &= i \frac{\partial Z}{\partial x} - \frac{2\omega}{\sigma} \frac{\partial Z}{\partial y}, \\ \frac{\sigma^2 - 4\omega^2}{g\sigma} V &= i \frac{\partial Z}{\partial y} + \frac{2\omega}{\sigma} \frac{\partial Z}{\partial x}, \end{aligned} \right\} \dots \dots (5.2)$$

where

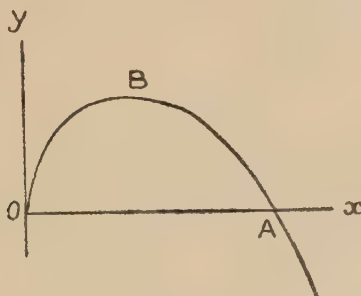
$$\kappa^2 = (\sigma^2 - 4\omega^2)/gh,$$

and ω is now constant.

Let us first apply (3.4) to a region bounded by the coast ABO and a straight line OA (fig. 3). We shall show that

when we know the tidal elevation on the coast we can calculate both the elevation and the normal current at all points along OA.

Fig. 3.



Take axes as shown and first let

$$Z = \frac{i\kappa^2 l^2}{\mu_s} \cos sx \sin \mu_s y,$$

where s is a constant, and

$$\mu_s^2 = \kappa^2 - s^2.$$

This satisfies (5.1) and on OA makes

$$Z=0, \quad hN = -hV = \sigma l^2 \cos sx. \quad (5.31)$$

On applying (3.4) we obtain, if $OA=b$,

$$\int_0^b \zeta' \sigma l^2 \cos sx dx + \int_{ABO} h \zeta' N ds = i\sigma \iint \zeta Z dS. \quad (5.32)$$

Now suppose that $b = m\pi/s$ where m is any integer. Then

$$\int_0^b \zeta' \sigma l^2 \cos sx dx = \frac{m}{s} \sigma l^2 \int_0^\pi \zeta' \cos m\xi d\xi, \quad (5.33)$$

and gives the coefficient of a Fourier's cosine-series for ζ' along OA. As m is at our disposal, we thus see that we can calculate the terms of this series when we know ζ over the sea and ζ' round the coast.

Next take

$$\frac{Z}{l} = \cos sx \cos \mu_s y + \frac{2\omega s}{i\sigma \mu_s} \sin sx \sin \mu_s y, \quad (5.41)$$

which also satisfies (5.1). On OA this makes

$$Z = l \cos sx, \quad hN = -hV = 0, \quad (5.42)$$

so that on substituting into (3.4) we obtain

$$\int_{ABO} h \zeta' N ds - \int_0^b h v l \cos sx dx = i\sigma \iint \zeta Z dS. \quad (5.43)$$

Again,

$$\int_0^b h\nu l \cos sx dx = \frac{m}{s} lh \int_0^\pi \nu \cos m\xi d\xi, \quad (5.44)$$

and we see that we can evaluate the terms of the Fourier's cosine-series for ν on OA.

To illustrate the formulæ of § 4 let us take

$$Z = \frac{1}{4} i \kappa^2 l^3 K_0(\kappa r) \quad (5.51)$$

where $K_0(\quad)$ denotes the Bessel's function of zero order and second kind. This makes the radial and transverse components of the vector (hU , hV) respectively equal to

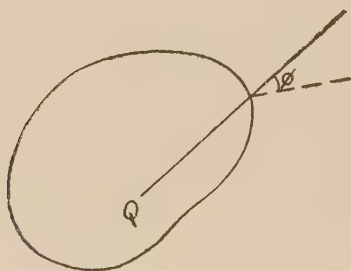
$$-\frac{1}{4} \sigma l^3 \frac{\partial}{\partial r} K_0(\kappa r), \quad -\frac{1}{4} \sigma l^3 \frac{2\omega}{i\sigma} \frac{\partial}{\partial r} K_0(\kappa r), \quad (5.52)$$

and therefore the value of hN is given by

$$-\frac{1}{4} \sigma l^3 \left\{ \cos \phi - \frac{2\omega}{i\sigma} \sin \phi \right\} \frac{\partial}{\partial r} K_0(\kappa r), \quad (5.53)$$

where ϕ is the angle between the outward drawn normal

Fig. 4.



and the radius vector from Q (fig. 4). The expression (5.53) may equally well be written

$$-\frac{1}{4} \sigma l^3 \left(\frac{\partial}{\partial n} - \frac{2\omega}{i\sigma} \frac{\partial}{\partial s} \right) K_0(\kappa r). \quad (5.531)$$

Equation (4.2) then takes the form

$$4\xi'_Q = - \int \left\{ \xi' \left(\frac{\partial}{\partial n} - \frac{2\omega}{i\sigma} \frac{\partial}{\partial s} \right) - \frac{\kappa^2}{i\sigma} h\nu \right\} K_0(\kappa r) ds + \kappa^2 \iint \xi \bar{\xi} K_0(\kappa r) dS. \quad (5.54)$$

If we next suppose that the sea is non-rotating so that

$\omega=0$ and

$$h\nu = \frac{i\sigma}{\kappa^2} \frac{\partial \xi'}{\partial n},$$

equation (5.54) becomes

$$4\xi'_Q = - \int \left\{ \xi' \frac{\partial}{\partial n} K_0(\kappa r) - K_0(\kappa r) \frac{\partial \xi'}{\partial n} \right\} ds + \kappa^2 \iint \bar{\xi} K_0(\kappa r) dS. \quad (5.541)$$

If we still further restrict by supposing that there are no disturbing forces, so that $\bar{\xi}=0$, we obtain a result given by Lamb* except that we have taken $K_0(\kappa r)$ instead of $D_0(\kappa r)$. The use of the real function $K_0(\kappa r)$ instead of the complex function $D_0(\kappa r)$ is legitimate when the region under consideration does not extend to infinity, as the two functions only differ by an imaginary multiple of $J_0(\kappa r)$ which has no sources in any finite region. We thus see that (4.2) is a generalization of the formula given by Lamb so as to cover the extra circumstances of curvature and rotation of the Earth, variable depth and the action of disturbing forces.

The integral equation (4.3) takes the form

$$2\xi'_Q + \int \xi' \left(\cos \phi - \frac{2\omega}{i\sigma} \sin \phi \right) \frac{\partial}{\partial r} K_0(\kappa r) ds = \frac{\kappa^2}{i\sigma} \int h\nu K_0(\kappa r) ds + \kappa^2 \iint \bar{\xi} K_0(\kappa r) dS. \quad (5.55)$$

Now the principal part of $\partial K_0(\kappa r) / \partial r$ as $r \rightarrow 0$ is $-2/\pi r$, and we see that all the integrals are convergent, except that containing $\sin \phi$ as a factor, which is semi-convergent. From the way in which the equation was obtained it is clear that we must interpret this integral as the limit of that obtained by excluding an arc of centre Q, when the length of this arc tends to zero, *i. e.* as the "principal value" in Cauchy's sense.

6. Ocean of Uniform Depth.

Suppose that

$$\left. \begin{aligned} \frac{4\Omega^2 a^2}{gh} \frac{U}{\sigma a} &= -iU_r \cdot \sin^{r-1} \theta \cdot e^{-is\chi} \\ \frac{4\Omega^2 a^2}{gh} \frac{V}{\sigma a} &= -V_r \cdot \sin^{r-1} \theta \cdot e^{-is\chi} \\ \frac{Z}{h} &= Z_r \cdot \sin^r \theta \cdot e^{-is\chi} \end{aligned} \right\}, \quad (6.1)$$

* 'Hydrodynamics,' Art. 305.

where U_r , V_r , Z_r are functions of θ only, and r , s are numerical constants.

It is found* that both for $r=s$ and $r=-s$ solutions of (3.1), (3.2) exist which make U_r , V_r , Z_r finite at the Equator and the North Pole. We shall fix their magnitudes by supposing that $U=1$ when $\theta=0$.

When $r=s$ we shall call the solution

$$U_s^+, V_s^+, Z_s^+,$$

and when $r=-s$ we shall call the solution

$$U_{-s}^-, V_{-s}^-, Z_{-s}^-.$$

It is to be noticed that in the above s may be either positive or negative.

Let us suppose that an ocean does not extend to the North Pole, and let us consider only that part of it which lies to the north of co-latitude α ($\leq \frac{1}{2}\pi$). Let us also suppose that the parallel of co-latitude α strikes the coast at $\chi=0$ and $\chi=m\pi/s$, m being an integer which determines s .

Now consider the solution of (3.1), (3.2), in which

$$\begin{aligned} \frac{gh}{4\Omega^2 a^2} \frac{Z}{h} = & \frac{1}{2} i e^{-is\chi} \frac{\sin^s \theta Z_s^+ / p_s - \sin^{-s} \theta Z_{-s}^- / q_{-s}}{P_s / p_s - Q_{-s} / q_{-s}} \\ & + \frac{1}{2} i e^{is\chi} \frac{\sin^{-s} \theta Z_{-s}^+ / p_{-s} - \sin^s \theta Z_s^- / q_s}{P_{-s} / p_{-s} - Q_s / q_s}, \quad (6.21) \end{aligned}$$

where

$$p_s, p_{-s}, q_s, q_{-s}$$

denote respectively the values of

$$\sin^s \theta \cdot Z_s^+, \sin^{-s} \theta \cdot Z_{-s}^+, \sin^s \theta \cdot Z_s^-, \sin^{-s} \theta \cdot Z_{-s}^-$$

for $\theta=\alpha$, and

$$P_s, P_{-s}, Q_s, Q_{-s}$$

denote respectively the values of

$$\sin^{s-1} \theta \cdot U_s^+, \sin^{-s-1} \theta \cdot U_{-s}^+, \sin^{s-1} \theta \cdot U_s^-, \sin^{-s-1} \theta \cdot U_{-s}^-$$

for $\theta=\alpha$. We shall then have for $\theta=\alpha$

$$Z=0, U=\sigma a \cos s\chi.$$

On applying (3.4) we therefore obtain

$$\int_0^{m\pi/s} h\zeta' \cdot \sigma a \cos s\chi \cdot a \sin \alpha d\chi + \int h\zeta' N ds = i\sigma \iint \zeta Z dS, \quad (6.22)$$

where the line-integral is taken round the coast of the ocean

* See G. R. Goldsbrough, Proc. Lond. Math. Soc. (2) xiv. pp. 31-66.

and the surface-integral over the surface of the ocean, in each case north of $\theta = \alpha$ only.

Now

$$\int_0^{m\pi/s} h\zeta' \sigma a \cos s\chi \cdot a \sin \alpha d\chi = \frac{m\sigma a^2 h \sin \alpha}{s} \int_0^\pi \zeta' \cos m\xi d\xi,$$

and we thus have the coefficient of a Fourier's cosine-series for ζ' along the parallel of co-latitude α . As m is at our disposal we can thus evaluate ζ' along any parallel of latitude when we know its values round the coast, and those of $\bar{\zeta}$ over the ocean.

Again, when

$$\begin{aligned} \frac{Z}{h} = & \frac{1}{2} e^{-is\chi} \frac{\sin^s \theta Z_s^+ / P_s - \sin^{-s} \theta Z_{-s}^- / Q_{-s}}{p_s / P_s - q_{-s} / Q_{-s}} \\ & + \frac{1}{2} e^{is\chi} \frac{\sin^{-s} \theta Z_{-s}^+ / P_{-s} - \sin^s \theta Z_s^- / Q_s}{p_{-s} / P_{-s} - q_s / Q_s}, \quad (6.31) \end{aligned}$$

we have

$$Z = h \cos s\chi, \quad hU = 0,$$

on $\theta = \alpha$, so that (3.4) will yield

$$\int h\zeta' N ds - \int_0^{m\pi/s} h\nu \cdot h \cos s\chi \cdot a \sin \alpha d\chi = i\sigma \iint \zeta Z dS, \quad (6.32)$$

the integrals being taken as in (6.22). Again, we see that we can evaluate ν through its Fourier's series along any parallel of latitude.

LXII. On *Kinematics*.

By CHARLES L. R. E. MENGES*.

THE following concerns the modern views related to electromagnetism. This subject being treated so clearly and concisely in Prof. J. H. Jeans' well-known excellent book†, a quotation therefrom will be the best beginning to attach my explanations

Page 607 reads:—"In Fizeau's water-tube experiment, a stream of water was made to flow through a tube, its velocity of flow being u relative to the earth, and a ray of

* Communicated by the Author.

† J. H. Jeans, 'The Mathematical Theory of Electricity and Magnetism' 4th edition (Cambridge, at the University Press, 1923).

light was passed through the water in the direction of its motion. To an observer moving with the stream, the water would appear to be at rest, so that the light would be propagated relatively to this observer with a velocity u' connected with the refractive-index ν of the water by the relation (C =velocity of light in vacuo)

$$u' = \frac{C}{\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

"According to classical laws of kinematics, the light ought to travel, relative to an observer at rest on the earth, with a velocity

$$u' + u \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{or} \quad \frac{C}{\nu} + u. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

"Fizeau found it possible to measure the actual velocity by an interference method and formula (3) was not confirmed. The formula

$$\frac{C}{\nu} + u \left(1 - \frac{1}{\nu^2} \right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

was found to represent the velocity accurately both for water and other transparent media."

The generally admitted inference is :—

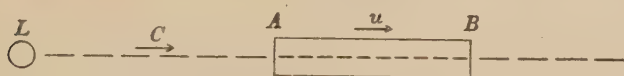
By applying the laws of kinematics to Fizeau's water-tube experiment, formula (3) is obtained, and this formula was not confirmed by experiments. Therefore those laws of kinematics are not true.

This conclusion is derived from results obtained by means of a moving *liquid*, water, which has obvious practical advantages for the experiment. But the theory, the kinematical insight of the question, is more intricate when the light-waves propagate in a *motionless* tube, wherein water flows, than when they traverse a moving *solid* transparent substance. It is therefore of importance, that formula (4) for flowing water has been very accurately confirmed indirectly by Prof. P. Zeeman's experiments on Fizeau's effect in moving *solid* transparent substances*.

The following concerns in particular Fizeau's effect in moving transparent *solids*.

* P. Zeeman, *Verslagen Akadem. Amsterdam*, xxvii. p. 1453 (1919).

In Zeeman's experiment the source of light L sends a ray through a glass cylinder AB moving with the velocity u relative to L. When the glass cylinder is still at rest, the frequency n^0 of the light-waves in it is the same as in the



source L. Then the light-waves propagate with velocity u^0 in the glass, its refractive index being ν^0 according to the relation

$$u^0 = \frac{C}{\nu^0}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

We know that the refractive index of glass, when at rest, varies with the frequency of the light-waves. The frequency in the glass being n instead of n^0 , the refractive index is by Lorentz's formula * :

$$\nu = \nu^0 + (n - n^0) \frac{d\nu^0}{dn^0}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

When the frequency of the source L remains n^0 , but the glass is moving with velocity u in the direction of the propagating light-waves, then the frequency in the glass is no longer n^0 . By Doppler's effect it is then

$$n = n^0 \frac{C - u}{C}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Lorentz improved Fresnel's original formula with ν^0 , by replacing ν^0 by ν from equation (6). The velocity u may be introduced in equation (6) by replacing $n - n^0$ by its value from equation (7). But it must be well understood that $\frac{d\nu^0}{dn^0}$ in equation (6) is not in the least related with movement ; its value is taken from experiments *without any material movement*. Therefore, with ν according to equation (6) instead of ν^0 , only a difference in frequency *apart from motion* is taken into account, but not that part of the observed total effect, which in particular results from motion.

To discuss the question clearly, three exactly defined cases will be considered.

CASE 1 : The source of light L with frequency n^0 and the glass cylinder *at rest* ; the frequency in the glass is also n^0 .

CASE 2 : *Without material movement* as in case 1, but the

* H. A. Lorentz, 'The Theory of Electrons,' p. 191 ; and note 69, p. 316 (B. G. Teubner, Leipzig, 1909).

frequency of the source L and in the glass AB both being now n instead of n^0 .

CASE 3 : As in case 2 the frequency of the light-waves is n in the glass AB, which, however, is now moving away from L with velocity u .

In this last case with the moving glass cylinder (Zeeman's experiment), the frequency in the source of light L must differ from n because of Doppler's effect. But immediate action at a distance is excluded, therefore the different frequency in L cannot *by itself* produce in the distant glass cylinder AB an effect differing from that in case 2. As experiment proves beyond any doubt that the optical effect in case 3 is really different from that in case 2, there must exist in the field, immediately in contact with the glass face A, in case 3 something which differs from that in case 2. Now, in case 2 *without material motion*, the velocity of the light-waves which fall on the face A is C. But in case 3 the face A is moving with velocity u relative to its position in case 2, where it receives the waves with velocity C. Therefore in case 3 the speed wherewith the moving face A receives the waves is *by kinematics* equal to $C-u$.

This being taken into account, I showed * by pure mathematics and kinematics, without introducing a "dragging coefficient" or any hypothesis of that kind, that ν in formula (1)—to make it kinematically correct for a moving substance be it water or glass—must be replaced by

$$\nu' = \nu - \frac{u}{C}(\nu^0 - 1). \quad (8)$$

The true formula for u' in moving glass is then

$$u' = \frac{C-u}{\nu'} = \frac{C-u}{\nu - \frac{u}{C}(\nu^0 - 1)}. \quad (1a)$$

It is now easy to explain the above given quotation : "Fizeau found it possible to measure the actual velocity and formula (3) was not confirmed."

For formula (3), namely

$$\frac{C}{\nu} + u, \quad (3)$$

is obtained by inserting in formula

$$u' + u \quad (2)$$

the value of u' from

$$u' = \frac{C}{\nu}. \quad (1)$$

* *Comptes Rendus*, clxxv. p. 574 (1922).

Formula (2) being taken in accordance with perfectly true laws of kinematics, then it will certainly become false, if the true value of u' be replaced by a value which is contradictory with said laws. This is the case with formula (3), because of the false value of u' from equation (1), which ought to be true for the *moving* glass. But in this sense C in it is certainly inconsistent with the laws of kinematics, as I above explained; C must be replaced by $C-u$, giving the kinematically correct formula (1a).

Instead of the hitherto generally admitted inference that the laws of kinematics, as expressed in formula (2), are not correct, the true inference now is quite inverse. *For according to the laws of kinematics formula (1) must be replaced by formula (1a), and this is exactly confirmed by Zeeman's very accurate experiments.* It follows from the formula confirmed by Zeeman's experiments, his formula being obtainable from my new formulæ (1a) and (8) by pure mathematical transformations, as follows.

The glass cylinder of length l being at rest, the speed of the light-waves therein is $u^0 = \frac{C}{v^0}$, and it contains

$$l : \frac{u^0}{n^0} = \frac{ln^0}{u^0}$$

waves. While the glass cylinder moves it contains

$$\frac{ln}{u'}$$

waves. The optical effect of motion is therefore

$$l \left(\frac{n^0}{u^0} - \frac{n}{u'} \right),$$

and with u' from formula (1a) it is

$$l \left(\frac{n^0}{\frac{C}{v^0}} - \frac{n^0 \frac{C-u}{C}}{\frac{C-u}{v'}} \right) = \frac{ln^0}{C} (v^0 - v').$$

With formulæ (6), (7), (8) and the wave-length $\lambda = \frac{C}{n^0}$ this optical effect is

$$\frac{lu}{C} \left(v^0 - 1 - \lambda \frac{dv^0}{d\lambda} \right),$$

which is Zeeman's formula.

LXIII. *The Proof of the Corollary of Carnot's Theorem.*
By ARTHUR E. RUARK*.

THERE are many methods for proving by the use of the first and second laws of thermodynamics the theorem that "All reversible engines working between the same temperatures have equal efficiencies."

So far as I can find, it has not been pointed out that this statement may be derived by using the first law together with a postulate which *denies* the validity of the second law. This postulate may be stated in the form: It is impossible for any self-acting mechanism working in a complete cycle to produce work continuously by transferring heat from a higher to a lower level of temperature without producing any other effect.

Let us first consider the usual proof of this theorem. Let there be two reversible engines, 1 and 2, such that in a single cycle each does work W . Engine 1 takes in heat Q_1 from the hot bath and gives heat q_1 to the cold bath, while engine 2 takes in Q_2 and rejects q_2 . We have

$$Q_1 - q_1 = W = Q_2 - q_2,$$

whence

$$Q_1 - Q_2 = q_1 - q_2.$$

If engine 1 drives engine 2 in a reverse direction, the hot bath loses $Q_1 - Q_2$ and the cold bath gains $q_1 - q_2$. By the second law

$$Q_1 - Q_2 \geq 0.$$

But if engine 2 drives engine 1 reversely, we find in exactly similar manner that

$$Q_2 - Q_1 \geq 0.$$

Therefore $Q_1 = Q_2$, $q_1 = q_2$, and

$$\frac{W}{Q_1} = \frac{W}{Q_2}.$$

If we say, on the contrary, that the hot bath gains heat at the expense of the cold bath, we have in the first experiment

$$Q_1 - Q_2 \leq 0,$$

and in the second

$$Q_2 - Q_1 \leq 0,$$

leading to the same conclusion as before.

* Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

The interest lies in the fact that deductions from the theorem "All reversible engines working between the same temperatures have equal efficiencies" cannot be used as the basis of experiments designed to test the validity of the second law. It will be understood, of course, that the above objections do not apply to the theorem "A non-reversible engine cannot be as efficient as a reversible engine working between the same temperatures." It is only the preceding statement concerning all reversible engines which can be proved by postulating the opposite of the second law.

Bureau of Standards,
October 30, 1924.

LXIV. *The Influence of Temperature on the Intensity of Reflexion of X-Rays from Rocksalt.* By R. W. JAMES, M.A.,
*Senior Lecturer in Physics in the University of Manchester**.

CONTENTS.

1. Introductory.
2. Previous experimental work.
3. Description of experiments.
4. Permanent effects of heat on the reflecting power of rocksalt.
5. Results of observation.
6. Correction of observations.
7. Discussion of results and deduction of an empirical law to fit them.
8. Comparison with Debye's theory.

1. **A** THEORETICAL expression for the influence of temperature on the intensity of the interference maxima produced when X-rays are diffracted by a crystal was first obtained by Debye† in 1913. Suppose a beam of X-rays of wave-length λ passes through a crystal in a direction making a glancing-angle θ with a series of atomic planes whose spacing is d . Then the spectrum of the n th order may be considered as produced by reflexion at these planes, if

$$2d \sin \theta = n\lambda.$$

If the atoms lie exactly in the plane, the contributions from all of them to this spectrum will be exactly in phase; but if, by reason of their heat-motion, they are displaced by varying small amounts from these planes, the contributions

* Communicated by Prof. W. L. Bragg, M.A., F.R.S.

† P. Debye, *Verh. der deutsch. Phys. Ges.* xv. pp. 678, 738, and 867 (1913).

will no longer all be in phase, and the intensity of the spectrum will be correspondingly reduced. Debye in his earliest papers supposed each atom to be bound by a quasi-elastic force to a position of equilibrium lying in the atomic plane, or rather at one of the lattice points of the crystal. Owing to the heat motion, each atom is displaced at any instant by a certain distance from its equilibrium position. If we knew all the displacements at any time, we could calculate the effect on the intensity of the X-ray beam diffracted in any direction. Debye carried out the calculation for a given configuration, multiplying the intensity factor so obtained by the probability of the occurrence of the configuration, and summing up over all possible configurations obtained a value for the mean intensity of the diffracted beam in any direction. The probability of a given set of displacements was calculated according to Maxwell's distribution law. Debye obtained an expression for the intensity of the X-ray beam in any direction which consisted of two parts—the first corresponding to the scattered radiation, the second to the interference maxima. The effect of increasing temperature is to increase the scattered radiation and to diminish the intensity of the interference maxima. Debye's early calculation showed that to account for the effect of the temperature movement, the intensity of the scattered radiation had to be multiplied by a factor

$$\left(1 - e^{-\frac{16\pi^2 kT}{f\lambda^2} \sin^2 \frac{\phi}{2}}\right),$$

while that of the interference maxima had to be multiplied by a factor

$$e^{-\frac{16\pi^2 kT}{f\lambda^2} \sin^2 \frac{\phi}{2}},$$

where T is the absolute temperature, k the gas constant, f the quasi-elastic force per unit displacement of the atom, and ϕ the angle which the diffracted beam makes with the incident beam, so that if the spectrum is supposed to be formed by reflexion from a set of planes at a glancing angle θ , $\theta = \phi/2$.

The use of the Maxwell-Boltzmann distribution law in the above calculation is equivalent to assuming that the displacements of the atoms are all independent. It is evident, however, that this assumption is not justified. The atoms are not held to fixed points of equilibrium, but to one another, and the displacements of any atom must influence those of its neighbours. The heat-motion of such a medium

may be considered as a series of "elastic waves," and had been discussed by Born and Karman*. Debye† recalculated the effect of heat-motion on the interference maxima, using these ideas and taking the quantum theory into account. He found that the intensity of the interference maxima had to be multiplied by a factor e^{-M} , where

$$M = \frac{6h^2}{\mu k \lambda^2 \Theta} \cdot \sin^2 \frac{\phi}{2} \cdot \frac{\phi(x)}{x} \quad . \quad . \quad . \quad (1)$$

Here μ is the mass of one of the atoms, h is Planck's constant, Θ a temperature characteristic of the crystal, $x = \frac{\Theta}{T}$, and $\phi(x)$ is a certain function of $\frac{\Theta}{T}$ which can be evaluated. If the existence of Nullpunktsenergie is assumed, $\frac{\phi(x)}{x}$ is replaced by $\left\{ \frac{1}{4} + \frac{\phi(x)}{x} \right\}$. For values of T small compared with the characteristic temperature Θ , M should be proportional to T^2 , while for high values of T it should be proportional to T , as the more elementary treatment showed.

More recently the question of the effect of temperature on the scattered radiation has been considered by Faxen‡ and by Waller§.

2. The first experiments on the influence of temperature on the intensity of reflexion of X-rays by crystals were carried out in 1914 by Sir William Bragg||, who used rocksalt and sylvine. With rocksalt, experiments were made at temperatures of 15° and 370° C., and the conclusion was reached that the effect was of the same order as that calculated by Debye. More recently experiments on similar lines have been made by Backhurst¶, who used aluminium, corundum, carborundum, diamond, and graphite. Only very general agreement was found with the theory of Debye, but it must be noticed that Debye's theory applies to a simple cubic lattice only. Quite recently Collins** has studied the Debye effect for aluminium, and again finds results at variance with the theory of Debye. The

* Born and Karman, *Phys. Zeitschr.* xiv. p. 65 (1913).

† *Ann. der Phys.* xliii. p. 49 (1914).

‡ H. Faxen, *Zeitsch. für Physik.* xvii. p. 266 (1923).

§ L. Waller, *ibid.* p. 398 (1923).

|| W. H. Bragg, *Phil. Mag.* May 1914,

¶ Proc. Roy. Soc. A, cii. p. 340 (1922).

** E. H. Collins, *Phys. Rev.* xxiv. p. 152 (1924).

effect of temperature on the scattered radiation has been studied experimentally by G. E. M. Jauncey*.[‡]

3. The experiments to be described in the present paper had their origin in some work by Professor W. L. Bragg †, C. H. Bosanquet, and the writer on the intensity of reflexion of X-rays from rocksalt, in which an attempt was made to get some idea of the distribution of the electrons in the atoms of sodium and chlorine. In the course of this work it was necessary to make allowance for the Debye factor. The only figures available for rocksalt were those of Sir W. H. Bragg obtained in 1914, and it was considered desirable to repeat them with the better apparatus at our disposal, and if possible to extend the temperature range in both directions. The intensities of reflexion were measured by the method first used by W. H. Bragg †, and described in detail by W. L. Bragg, James, and Bosanquet in the papers quoted. The crystal was mounted on the table of an ionization spectrometer. The ionization chamber was set at the angle appropriate to the spectrum under investigation, with a slit wide enough to receive the whole reflected beam, including both the α and α' peaks, and the crystal was rotated at a uniform angular velocity through the range of angles over which it reflected. The total quantity of electricity passing across the ionization chamber during the sweep of the crystal was measured. Let this be proportional to E . Then if ω is the angular velocity with which the crystal is swept, and I the quantity of electricity passing in unit time when the beam is allowed to enter the chamber directly, the quantity $\frac{E\omega}{I}$ is a constant for a given crystal face, and can be taken as a measure of the reflecting power of that face. The quantity $\frac{E\omega}{I}$ is called by Darwin the "integrated reflexion"—a convenient term which will be employed here.

The source of radiation was a Coolidge bulb with either a rhodium or a molybdenum anticathode. To supply the current, a transformer operated by a rotary converter of about 2.25 kilowatts capacity worked from the Corporation mains and producing alternating current at about 140 volts was used. The potential employed was usually about

* Jauncey, *Phys. Rev.* xx. p. 421 (1922).

† *Phil. Mag.* xli. p. 309 (1921); xlii. p. 1 (1921); xliv. p. 433 (1922).

‡ *Loc. cit.*

50,000 volts. With this arrangement it was found possible to keep the intensity of the X-ray beam far steadier than in the earlier experiments *, when a coil and mercury break were used. A null method was used in the observations. The string of the electrometer, which was of the Lutz-Edelmann type, was connected to the inner plate of a condenser, whose outer coating could be raised to any desired potential by means of a potential divider. The sign of the potential applied to the outer coating was such as to neutralize by induction the charge received by the electrometer due to the ionization current. The potential necessary to bring the string back to its zero is then proportional to the total charge received by the electrometer during the observation. The actual readings taken were thus the readings on the potential divider, which had one hundred divisions. A maximum potential of 6 volts could be applied, and to increase the range of reading, any desired fraction of the potential could be tapped off by means of a post-office box and applied to the potential divider. The range of the instrument could be increased still further by having several inner plates of different sizes for the condenser. In this way spectra differing greatly in their absolute intensity could be compared.

The crystal was held between two jaws lined inside with asbestos, on an iron stand to which the necessary adjustments for tilt and centring could be given. The stand was mounted on an asbestos sheet supported on brass and insulated from the spectrometer table by a fused silica ring 3 cm. in height packed with kieselguhr. Over the crystal fitted a cylindrical electric furnace wound with "nichrome" wire and provided with mica windows to allow the ingress and egress of the X-rays. The furnace was surrounded by a cylinder of sheet asbestos pierced with suitable openings, and radiation downwards to the spectrometer table was further checked by surrounding the silica tube, on which the furnace was mounted, by a broad collar of asbestos sheeting. The arrangement for heat insulation proved very satisfactory, and it was possible to work for hours with the crystal at red heat with the spectrometer table only slightly warm. The whole furnace, including the silica pedestal, could be lifted off the spectrometer table and replaced while hot, so that alternate readings with the heated crystal and with the standard could be made. It was found that no appreciable change in temperature was produced by

* Bragg, James, and Bosanquet, *loc. cit.*

removing the furnace from the spectrometer and placing it on another stand close beside it.

The temperature was measured by a thermocouple of iron-constantan placed in contact with the crystal face in such a position that the X-rays did not strike it. The e.m.f. generated by the couple was measured directly with a very convenient potentiometer, kindly lent for these experiments by the Cambridge and Paul Scientific Instrument Company, to whom my best thanks are due. The thermocouple and potentiometer were calibrated, using the boiling-point of water and the melting-points of tin, lead, zinc, antimony and aluminium, and from the readings so obtained a temperature-e.m.f. curve was drawn. Very closely similar curves were obtained with the different couples used, and the error in temperature should not be more than a few degrees. To ensure steadiness and uniformity of temperature, the crystal was heated for from one to two hours before readings were taken.

To determine the proper setting of the ionization chamber, which varies with the temperature on account of the expansion of the crystal and the consequent alteration in the spacing d , a series of readings were made in the region of the peak, the setting of the chamber being altered half a degree at a time, with a corresponding change in the crystal sweep. To determine the intensity of the peak, readings were taken with the chamber two degrees above and two degrees below the setting of the peak, where only the general continuous radiation from the bulb could enter it. The mean of these readings was subtracted from that corresponding to the peak, and the difference was taken as the intensity of the peak. The allowance for the general radiation is of considerable importance, since at high temperatures it may in some cases account for as much as 70 per cent. of the radiation entering the chamber at the setting of the peak. It should be noticed that any creep of the electroscope due to natural leak, or to scattered radiation, is included in the allowance for general. These factors remain practically constant as the intensity of the peak diminishes, and the increasing fraction of general radiation is no doubt largely due to this fact, although, in the case of high-order spectra, the general radiation will include reflexions of longer wavelength at lower orders, for which the decrease of intensity with temperature will be less than for the peak, and this also will cause an increase in the percentage of general as the temperature rises.

The intensity of reflexion from the crystal under investigation was compared in each case with the reflexion from the same face and the same order from a standard rocksalt crystal.

A typical comparison began with a determination of the percentage of general radiation for the heated crystal Q, and ended with a similar determination for the standard S. After the determination for Q, a series of alternate sets of readings at the peak-settings of Q and S were taken in rapid succession, Q being removed from the spectrometer and replaced by S, and so on. The mean values for Q and S obtained from these alternate readings are corrected by subtracting from each the appropriate percentage of general, and the ratio of the corrected values is taken as the ratio of the intensities of the two spectra.

4. Some difficulty was experienced in finding a crystal of rocksalt suitable for these experiments. It was found that all crystals which had a turbid appearance were destroyed on heating, owing to the swelling and bursting of the small liquid or gaseous inclusions which they contained. If care was taken to choose a perfectly clear crystal containing no inclusions, this difficulty could be overcome completely. Even with such crystals it was found that the intensity of reflexion became smaller after continued heating. A similar effect was noticed by Backhurst*, who ascribed it to the breaking down of one complete crystal into smaller ones differently oriented. It does not seem certain, however, that this is the true explanation, at any rate in the case of rocksalt; indeed, there is some reason to believe that the reverse may be true, and that the size of the homogeneous crystal elements may be increased by heating. The effect in question is much more marked with the first-order reflexion from the (100) face than with the second, and with the second it is more marked than with the third; and this appears to be the case whether the reflexion takes place from a face, or through a slip of crystal in the manner employed in determining the absorption coefficient at the reflecting angle †. For example, in some preliminary experiments with a slip of crystal about 1 mm. thick, the intensity (100) before heating was found to be 0.71 of the standard. After heating to 590° C., the intensity had fallen to 0.50 of the standard, but after the

* Backhurst, *Proc. Roy. Soc. A*, cii. p. 340 (1922).

† Bragg, James, and Bosanquet, *Phil. Mag.* July 1921, p. 1.

crystal had cooled, the intensity had only risen to 0.53. The intensity (200) before heating was 0.92; on heating to 590° it fell to 0.43 and rose on cooling to 0.83, and the permanent fall for (300) was still smaller. This behaviour suggests strongly that the effect of heating is to increase the special absorption or "extinction coefficient" of the crystal. This would have a far greater influence on the intensity of the strong (100) than on the weaker (200) and (300), and might be accounted for by a more perfect crystallization of the material of the slip. The effect is not confined entirely to the surface layers, since reflexion at a slip occurs throughout the whole thickness. The phenomenon requires investigation in much greater detail, and this work is being undertaken. Experiments showed that for (200) and spectra of higher orders, a steady state appears to be reached after several heatings to 500° or 600° . The values of the intensities are less by a few per cent. than those before heating, but are permanent in the sense that the intensities before heating and after heating, when the crystal has been allowed to cool again, are the same. No consistent values for (100) could be obtained, and consequently this spectrum was not used in the present set of experiments.

5. All the observations to be described were made by reflexion at a face. The first set of observations were made with the (300) spectrum, rhodium radiation being used. The rhodium anticathode contained ruthenium as an impurity, and the ruthenium lines caused a certain amount of trouble in determining the general radiation; so, later, the rhodium bulb was replaced by one having a molybdenum target, and with this a series of observations were made between 15° and 650° C., using the (200), (300), and (400) spectra. The results of the measurements are given in Table I.

In this table, column (1) gives the absolute temperature; column (2), R the intensity actually observed, expressed in terms of the reflexion from the corresponding face of the standard crystal at 19° C. as unity. Column (3) gives the ratio of R_T , the observed intensity, corrected in the manner described below, to R_1 the mean corrected intensity at room temperature.

TABLE I.

Rh $K\alpha$ radiation. $\lambda = 0.615 \text{ \AA}$.

	(1) T.	(2) R.	(3) $\frac{R_T}{R_1}$	(4) $T^2 \left(\frac{\sin \theta}{\sin \theta_1} \right)^2$	(5) $\log_{10} \frac{R_T}{R_1}$	(6) $\left(\frac{\lambda}{\sin \theta_1} \right)^2 \log_{10} \frac{R_T}{R_1}$
(300)	293	0.926	1.015	8.58×10^4	+0.0064	+0.022
$\theta_1 = 19^\circ 10'$	292	0.911	0.998	8.53 "	-0.0007	-0.002
$\sin \theta_1$	291	0.908	0.995	8.47 "	-0.0020	-0.007
$= 0.3283$	292	0.906	0.991	8.53 "	-0.0031	-0.011
	413	0.701	0.765	16.89 "	-0.1163	-0.438
	472	0.621	0.677	21.95 "	-0.1696	-0.597
	513	0.535	0.582	25.83 "	-0.2347	-0.826
	615	0.357	0.388	36.83 "	-0.4114	-1.447
	630	0.351	0.381	38.58 "	-0.4190	-1.474
	670	0.304	0.330	43.51 "	-0.4818	-1.695
	778	0.169	0.183	58.21 "	-0.7379	-2.596
	862	0.115	0.124	70.98 "	-0.9060	-3.188

Mo $K\alpha$ radiation. $\lambda = 0.710 \text{ \AA}$.

(200)	292	0.831	0.987	8.53×10^4	-0.0057	-0.045
$\theta_1 = 14^\circ 37'$	292	0.845	1.003	8.53 "	+0.0016	+0.013
$\sin \theta_1$	292	0.850	1.009	8.53 "	+0.0041	+0.032
$= 0.2524$	426	0.710	0.833	18.04 "	-0.0793	-0.628
	579	0.595	0.692	32.69 "	-0.1598	-1.265
	703	0.500	0.577	46.81 "	-0.2390	-1.892
	843	0.362	0.413	67.94 "	-0.3841	-3.040
	913	0.312	0.355	79.20 "	-0.4500	-3.562
(300)	291	0.917	1.000	8.47×10^4	0.000	0.000
$\theta_1 = 22^\circ 15'$	393	0.722	0.785	15.47 "	-0.1051	-0.370
$\sin \theta_1$	511	0.510	0.552	25.65 "	-0.2582	-0.908
$= 0.3786$	625	0.339	0.366	38.04 "	-0.4361	-1.535
	756	0.191	0.205	55.04 "	-0.6882	-2.422
	898	0.102	0.109	76.70 "	-0.9624	-3.387
(400)	292	0.943	0.989	8.53×10^4	-0.0046	-0.009
$\theta_1 = 30^\circ 18'$	290	0.964	1.012	8.41 "	+0.0050	+0.010
$\sin \theta_1$	382	0.682	0.714	14.47 "	-0.1466	-0.290
$= 0.5045$	437	0.504	0.527	18.87 "	-0.2784	-0.551
	503	0.362	0.378	24.36 "	-0.4228	-0.837
	593	0.219	0.228	34.30 "	-0.6426	-1.272
	697	0.110	0.114	46.97 "	-0.9436	-1.867

6. The measured intensity R is proportional to the integrated reflexion $\frac{E\omega}{I}$, where E is the total energy reflected when the crystal is rotated with angular velocity ω , and I is the energy received by the ionization chamber when the incident beam enters it for one second. Now it can be shown that *†

$$\frac{E\omega}{I} = \frac{N^2\lambda^3}{2\mu \sin 2\theta} \cdot \frac{e^4}{m^2c^4} \cdot F^2 \cdot \frac{1 + \cos^2 2\theta}{2} \cdot e^{-bf(T) \frac{\sin^2 \theta}{\lambda^2}}. \quad (2)$$

In this formula N is the number of molecules per unit volume of the crystal, μ the linear absorption coefficient of the crystal, θ the glancing angle of reflexion, and λ the wave-length of the X-rays. e and m are the charge and the mass of an electron, and c is the velocity of light. The factor $\frac{1 + \cos^2 2\theta}{2}$ allows for the fact that the incident rays are unpolarized, and the factor F^2 for the finite size of the atom—which, since the electrons producing the scattering of the X-rays are distributed throughout a region whose dimensions are comparable with the spacings of the atomic planes, adds to the spectra a contribution which depends on the angle of diffraction, becomes smaller as that angle increases, and is proportional to the number of electrons in the atom for very small angles of scattering‡. As the formula is written, the factor F^2 also includes the “structure factor” which depends on the arrangement of the atom in each repeat of the crystal pattern.

The term $e^{-bf(T) \frac{\sin^2 \theta}{\lambda^2}}$ is the Debye factor which is under investigation in this paper.

We may write

$$e^{-bf(T) \frac{\sin^2 \theta}{\lambda^2}} = \frac{E\omega}{I} \cdot \frac{4m^2c^4}{e^4\lambda^3} \cdot \frac{\mu}{N^2} \cdot \frac{\sin 2\theta}{1 + \cos^2 2\theta} \cdot \frac{1}{F^2} \propto R_T. \quad (3)$$

The measured intensity R , column (2), Table II., is proportional to $\frac{E\omega}{I}$. We require R_T , the corrected intensity, column (3), which is proportional to the value of the Debye factor at different temperatures. To obtain this it is

* C. G. Darwin, *Phil. Mag.* xxvii, pp. 315 and 675 (1914).

† A. H. Compton, *Phys. Rev.* ix, p. 1 (Jan. 1917).

‡ W. L. Bragg, James, and Bosanquet, *Phil. Mag.* xli, p. 309 (1921); xlii, p. 1 (1921); xlii, p. 433 (1922).

necessary to allow for the fact that μ , N , θ , and F all depend on the temperature; μ and N are proportional to the density of the crystal, which decreases as the temperature rises owing to the thermal expansion, and for the same reason θ , the glancing angle for a given spectrum, decreases as T increases. The factor F^2 depends on $\frac{\sin \theta}{\lambda}$, and thus on the temperature. The change of θ with temperature was determined by direct measurement, and from this the value for α the coefficient of expansion of the crystal was calculated. To a sufficient approximation for the purpose under consideration, the coefficient of expansion was found to be linear over the range from 0° to 500° . The value of α obtained as a mean of several experiments was 0.0000383, which is in fair agreement with that obtained by Fizeau, 0.0000402, over a much smaller range from interference measurements. From this figure, the ratios of the values of the factors $\frac{\mu}{N^2}$ and $\frac{\sin 2\theta}{1 + \cos^2 2\theta}$ at any temperature to those at room temperature were calculated directly.

The allowance for the change in F^2 presents more difficulties. The values of F^2 determined by W. L. Bragg, James, and Bosanquet* for rhodium rays were used. In order to apply these determinations to the observations made with molybdenum radiation, use was made of the fact that F is a function of $\frac{\sin \theta}{\lambda}$. If the values of F^2 obtained for rhodium radiation are plotted against $\frac{\sin \theta}{\lambda_{\text{Rh}}}$, the curve obtained should be independent of the wavelength, and the value of F^2 for any angle θ for molybdenum can be read off at once over the corresponding value of $\frac{\sin \theta}{\lambda_{\text{Mo}}}$. The uncertainty in this correction lies in the uncertainty of the actual values of F^2 , which change rapidly with θ . The corrections for $\frac{\mu}{N^2}$ and for $\frac{1}{F^2}$ go in opposite directions, so that the total correction is not large and was not over 2 per cent. in any case, which is really within the errors of experiment.

There is one other correction to be taken into account—that for the change in the “extinction coefficient.” For intense spectra the value of the linear absorption coefficient

* Phil. Mag. xlii. p. 1 (1921).

depends on the intensity of the spectrum*; hence, as the intensity diminishes with rising temperature, the effective value of μ decreases. It has been shown that, to a fair degree of approximation,

$$\mu = \mu_0 + \epsilon = \mu_0 + kR, \quad . \quad . \quad . \quad . \quad (4)$$

where μ is the effective absorption coefficient at the reflecting angle, μ_0 is the ordinary absorption coefficient of the crystal, and ϵ is the extinction coefficient, which is proportional to the observed intensity of reflexion. The values of ϵ for different spectra for rhodium radiation were determined in the paper quoted. More recently, Wasastjerna† has carried out a determination by a different method for molybdenum radiation, and this has been employed in the present paper. Wasastjerna finds that $\mu_0 = 16.2$ and $\epsilon = 4.4$ for (100). Assuming as a sufficient approximation that $R_{100} : R_{200} : R_{300} = 100 : 20 : 5$, we can, using (4), obtain a curve giving the value of ϵ for different values of R , and so apply the necessary correction.

The extinction correction is inappreciable for the 3rd- and 4th-order spectra, and has only been applied in the case of (200). The allowance for extinction made above is very uncertain. It is known that the extinction coefficient depends considerably on the particular crystal used, and, as we have seen, it is possible that the extinction coefficient for a rocksalt crystal which has been heated is abnormally large. All that can really be claimed is that the results corrected in the manner described are probably closer to the truth than they would have been had no correction been applied at all. In any case, the correction for the (200) spectrum is not very large.

7. The values of the corrected reflexion $\frac{R_T}{R_1}$, plotted against the absolute temperature, are shown in fig. 1.

The theory of Debye leads to the conclusion that if R_T is the corrected reflexion at temperature T ; R_1 that at any standard temperature T_1 (here the room temperature); and R_0 the value of the reflexion at absolute zero, then

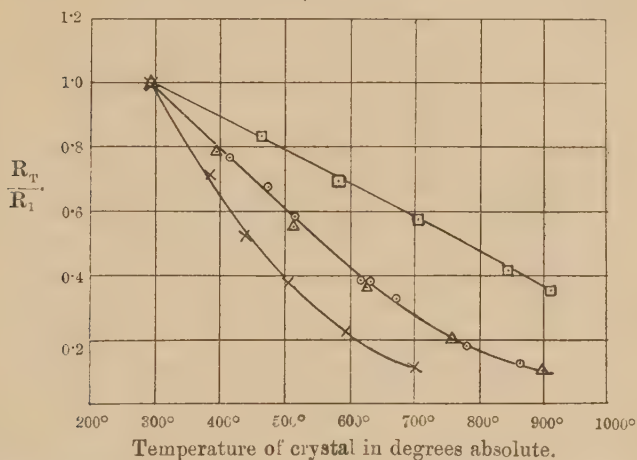
$$\left. \begin{aligned} R_T &= R_0 \exp \left\{ -bf(T) \frac{\sin^2 \theta}{\lambda^2} \right\}, \\ R_1 &= R_0 \exp \left\{ -bf(T_1) \frac{\sin^2 \theta_1}{\lambda^2} \right\}, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (5)$$

* Bragg, James, and Bosanquet, *Phil. Mag.* xlii. p. 1 (1921).
C. G. Darwin, *Phil. Mag.* xliii. p. 800 (1922).

† W. A. Wasastjerna, *Soc. Sci. Fenn.* ii. p. 15.

where b is a constant, $f(T)$ some function of the absolute temperature, and θ and θ_1 the glancing angles at T and T_1 respectively.

Fig. 1.



○ (300) Rhodium radiation. Δ (300) Molybdenum radiation.
 ◻ (200) Molybdenum radiation. × (400) " "

Hence

$$\frac{R_T}{R_1} = \exp \left\{ -\frac{b}{\lambda^2} (f(T) \sin^2 \theta - f(T_1) \sin^2 \theta_1) \right\}$$

$$= \exp \left[-\frac{b \sin^2 \theta_1}{\lambda^2} \left\{ f(T) \left(\frac{\sin \theta}{\sin \theta_1} \right)^2 - f(T_1) \right\} \right], \quad \dots \quad (6)$$

$$= \text{const.} \times \exp \left\{ -\frac{bn^2}{4d_1^2} f(T) \left(\frac{\sin \theta}{\sin \theta_1} \right)^2 \right\}, \quad \dots \quad (7)$$

where n is the order of the spectrum and d_1 the spacing of the atomic planes at the standard temperature T_1 . Thus the curve showing the relationship between $\frac{R_T}{R_1}$ and T should be independent of the wave-length for a given order, apart from the effect introduced by the small change in the value of $\left(\frac{\sin \theta}{\sin \theta_1} \right)^2$ as the temperature changes.

This portion of the theory is confirmed by the experiments. The curve in fig. 1 for the (300) spectrum was obtained with both rhodium and molybdenum radiation. The circles indicate the points obtained with rhodium

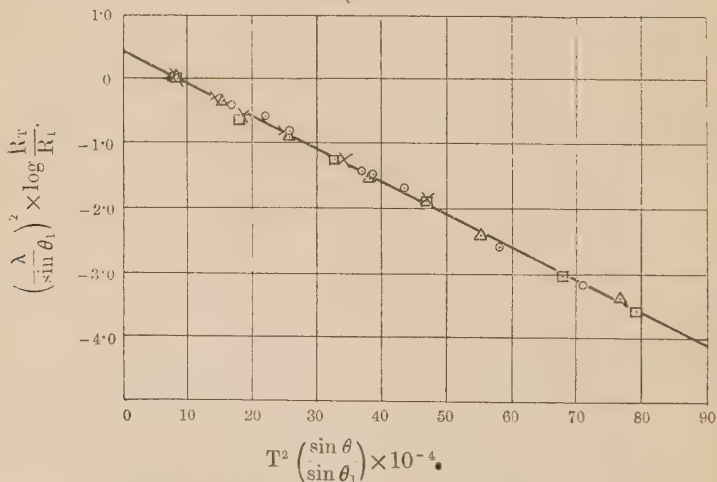
radiation, the triangles those with molybdenum, and it will be seen that both sets of points lie on the same curve, almost within the limits of experimental error.

To find the form of $f(T)$ which agrees most closely with the observations, we write equation (6) in the form

$$\left(\frac{\lambda}{\sin \theta_1}\right)^2 \log_e \frac{R_T}{R_1} = -bf(T) \left(\frac{\sin \theta}{\sin \theta_1}\right)^2 + \text{const.} \quad (8)$$

Thus, if $\left(\frac{\lambda}{\sin \theta_1}\right)^2 \log \frac{R_T}{R_1}$ is plotted against $f(T) \left(\frac{\sin \theta}{\sin \theta_1}\right)^2$, all the points should lie on the same straight line, whatever the order of the spectrum observed, and whatever the wavelength. Debye's theory indicates that $f(T)$ should be proportional to T , but if $\log \frac{R_T}{R_1}$ is plotted against T , not even an approximately straight line is obtained. If, however, we plot $\left(\frac{\lambda}{\sin \theta_1}\right)^2 \log \frac{R_T}{R_1}$ against $T^2 \left(\frac{\sin \theta}{\sin \theta_1}\right)^2$, all the 33 experimental points lie very nearly indeed on a straight line. This curve is shown in fig. 2, where the circles, triangles, squares, and crosses correspond to those in fig. 1.

Fig. 2.



○ (300) Rhodium radiation.

△ (300) Molybdenum radiation.

□ (300) Molybdenum radiation.

× (400) " "

The fact that all the points lie on the same line means that the exponent of the Debye factor is proportional to $\frac{\sin^2 \theta}{\lambda^2}$

for all the spectra investigated; while the fact that a straight line is obtained when $f(T)=T^2$ means that we can write the factor

$$e^{-bT^2 \frac{\sin^2 \theta}{\lambda^2}}.$$

Calculating, by the method of least squares, the most probable straight line in fig. 2, we obtain

$$R_T = R_0 e^{-1.162 \times 10^{-5} \frac{\sin^2 \theta}{\lambda^2} \cdot T^2},$$

where λ is expressed in Ångström units, as the empirical expression which fits the experimental results most closely.

8. We have seen that, according to the theoretical work of Debye, the exponent M in the temperature factor should be given by

$$-M = \frac{6h^2}{\mu k \Theta} \sin^2 \theta \frac{\phi(x)}{x},$$

where $x = \frac{\Theta}{T}$, and Θ is the "characteristic temperature" which for rocksalt is 280° absolute. For values of T small compared with Θ this reduces, according to Debye, to

$$-M = \frac{\pi^2 h^2}{\mu k \Theta^3} \sin^2 \theta T^2; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

while for high temperatures

$$-M = \frac{6h^2}{\mu k \Theta^2} \frac{\sin^2 \theta}{\lambda^2} \cdot T. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The experimental results show that M is actually proportional to $\frac{\sin^2 \theta}{\lambda^2}$, and this would appear to indicate that the observations are reasonably accurate, and also that the allowance for general radiation has been made correctly, for the proportion of general to characteristic radiation is very different for the different spectra examined, and different also for the same spectra in the case of rhodium and molybdenum radiations.

But the results do not agree in the least with theory as to the form of the function of the temperature contained in M . Over the range of temperature considered, M should be proportional to T , whereas the results showed that with a fair degree of accuracy it is proportional to T^2 , which according to the theory should only be the case for temperatures up to about 50° absolute.

For high temperatures the form of M is the same as that obtained in the elementary treatment, from which

$$-M = \frac{16\pi^2 k}{f} \frac{\sin^2 \theta}{\lambda^2} T,$$

where f is the force called into play when the atom is displaced by unit distance from its equilibrium position. Comparison shows then that

$$\frac{f}{\mu} = \frac{8\pi}{3} \frac{k^2}{h^2} \Theta^2,$$

or that the restoring force f is proportional to the square of the characteristic temperature.

If we take

$$\Theta = 280^\circ,$$

$$h = 6.55 \times 10^{-27} \text{ erg. sec.},$$

$$k = 1.39 \times 10^{-16},$$

$$\mu = \text{average mass of an atom in the structure}$$

$$= 4.85 \times 10^{-23} \text{ gm.},$$

we obtain for the case applicable to high temperatures

$$-M = 4.89 \times 10^{-3} \frac{\sin^2 \theta}{\lambda^2} \cdot T, \quad . \quad . \quad . \quad (11)$$

λ being expressed, as before, in Ångström units. For (300) this reduces to

$$-M = 1.39 \times 10^{-3} T. \quad . \quad . \quad . \quad . \quad (12)$$

TABLE II.

T.	$\frac{R_T}{R_1}$ (calc.).	$\frac{R_T}{R_1}$ (obs.).
300°	.973	.98
400°	.846	.79
500°	.735	.60
600°	.640	.42
700°	.558	.27
800°	.486	.17
900°	.422	.10

Table II. shows the values of $\frac{R_T}{R_1}$ calculated from this formula compared with those actually observed. It is evident that the intensity of the spectrum falls off far more

rapidly with increasing temperature than theory indicates. The difference between the observed and calculated figures is much greater than could be accounted for by experimental errors, and there must therefore be some factor which diminishes the intensity as the temperature rises which has not been allowed for in the theory.

One possibility which might be worth examining is that the value of the factor F may depend on the temperature. The theory treats the atoms as diffracting points. Now we know that the atom does not diffract even approximately as a point, particularly for large values of θ . The electrons are distributed around the atomic nuclei throughout a region whose dimensions are comparable with the spacing of the crystal planes; this causes a rapid decrease in the effective scattering power of the atom as it increases, and the factor F is introduced to allow for this. If, owing to the temperature vibration and the consequent jostling of atom against atom, the electron orbits were caused to vibrate about their mean positions, this would cause a change in the factor F in such a direction as to increase the falling-off of intensity with temperature.

Another possibility, although it seems very unlikely that it could account for such a large effect as that observed, is that the crystal may become softer as the temperature rises, so that an atom is more easily displaced from its position of rest. This would be equivalent to supposing that the characteristic temperature Θ depends on the temperature—an hypothesis which might be investigated by examining the Reststrahlen at different temperatures. To account for the T^2 law on this hypothesis alone, it would have to be assumed that Θ varied as $\frac{1}{\sqrt{T}}$. This seems highly improbable, and it is more

likely that several factors work together and produce, over the range of temperature used, a law approximating closely to the T^2 law.

It is evidently desirable to extend the measurement to low temperatures, and experiments by means of which it is hoped to measure the intensity of reflexion at liquid-air temperature are already in progress.

Another point to be noticed is that in rocksalt we have two different kinds of atom—sodium and chlorine. In all the spectra so far examined we are dealing with the sum of the contributions from Na and Cl. In the case of spectra such as (111), (333), (311), (555), and so on we are, however, dealing with the difference of the contributions from

Na and Cl. It is proposed, therefore, to make a set of observations using the (333) spectrum, in order to see whether the law still holds good in this case.

In conclusion, I wish to express my thanks to Professor W. L. Bragg, F.R.S., for his interest and advice during the course of the work, and to Mr. W. A. Wood, B.Sc., for help with a number of the observations. My thanks are also due to Mr. W. Kay and Mr. W. Reynolds for much assistance in the design and construction of the apparatus. The X-ray bulb used in this research was very kindly presented to the laboratory by the General Electric Company of Schenectady, New York, and the alternator was purchased with the aid of a grant made by Messrs. Brunner Mond, Ltd.

Summary.

1. A series of measurements of the intensity of reflexion of X-rays from the (100) face of a rocksalt crystal at temperatures between 19° C. and 650° C. are described. The spectra investigated were the 2nd, 3rd, and 4th orders, using molybdenum $K\alpha$ radiation, and the 3rd order, using rhodium $K\alpha$ radiation.

2. A theoretical formula obtained by Debye shows that if R_T is the intensity of a spectrum reflected at a glancing angle θ at absolute temperature T ; R_0 that at absolute zero :

$$R_T = R_0 e^{-bf(T) \frac{\sin^2 \theta}{\lambda^2}} = e^{-M},$$

where b is a constant and $f(T)$ is some function of the temperature. The theory indicates further that over the range of temperature employed, M is of the form

$$-aT \frac{\sin^2 \theta}{\lambda^2}.$$

3. The experiments show that M is proportional to $\frac{\sin^2 \theta}{\lambda^2}$ for all the spectra investigated, but that instead of being proportional to T it is proportional to T^2 . The results obtained may be expressed by the empirical formula

$$R_T = R_0 e^{-1.162 \times 10^{-6} \frac{\sin^2 \theta}{\lambda^2} T^2},$$

where λ is expressed in Ångström units.

The intensity diminishes as the temperature rises much more rapidly than theory indicates.

The University, Manchester,
Jan. 28, 1925.

LXV. *Adsorption from the Gas Phase at a Liquid-Gas Interface.*—Part III. By THOMAS IREDALE*.

IN attempting to measure the surface tension of mercury in a vacuum by the drop method (Phil. Mag. xlviii. p. 189, 1924) certain difficulties were experienced owing to the rapid accumulation of impurities on the surface. In air, the surface tension was always higher than in a vacuum, except when it was measured with great rapidity in the vacuum, and also, in special cases, when the apparatus was newly cleaned and freshly-distilled mercury employed. It has been found very difficult to ascertain the exact nature of these impurities in every case, but it seems impossible now to believe in the suggestion originally made, that the anomalies observed are due to the presence of water films on the mercury surface. Difficulties of a similar kind have been experienced in the lubrication experiments of Hardy and co-workers (Phil. Mag. xxxviii. p. 32, 1919; Proc. Roy. Soc. A, c. p. 550, 1922), and are as likely as not due to adsorbed films, not necessarily derived from the vapour phase, which cannot be removed at ordinary temperatures even in the highest possible vacuum. In the washing and cleaning of glass apparatus with the usual reagents, certain impurities may sometimes be left behind on the glass which can only be removed by a more drastic method of rubbing or polishing of the glass surface. Such a procedure, however, would be very difficult with apparatus consisting of long capillary tubes, and this is probably one of the most serious defects in the original drop-weight apparatus designed by the author. The mercury column has to move against the interior glass surface of the capillary before issuing in drops from the orifice, and the chances of contamination in this way are very great. The possibility also of the electrification of the mercury by friction against the glass cannot entirely be ignored, but the earthing of the mercury in many instances has not changed the essential aspects of the phenomenon. It is remarkable that the presence of the air should so greatly hinder the adsorption of the impurities, but this does not seem to be a reversible effect; reversible, in the sense that the admission of air to a surface already

* Communicated by Prof. F. G. Donnan, F.R.S.

formed in the vacuum does not appear to result in a desorption of the impurities. It must be admitted, however, that the technique of the drop method is not sufficiently adaptable to the measurement of such reversible effects. What is needed is some method of measuring the surface tension of mercury which can be applied to both old and new surfaces. We could find the tension from the contour of a surface formed in a vacuum, and note how it changed on admission of air. If the change in shape pointed to an increase in the tension, we would be justified in saying that the effect was a reversible one. But in the drop method, the drop usually detaches before the air can be properly admitted to the dropping chamber, owing to vibration and similar causes; and this technical imperfection makes it difficult to say what one is actually measuring in many cases. Such vibration may be induced by the surging of the gas molecules as the air fills the vacuous space, and the drop will always detach at the point of maximum instability. We should not be justified in saying, therefore, that the adsorption of the impurities was irreversible, as the growth of the drop might be hindered owing to other extraneous causes. The drop method, then, is at best a dynamical one, and cannot be employed for accurately measuring reversible adsorption effects.

Another difficulty with the drop apparatus is the breaking apart of the mercury column in the capillary which is probably due to some minute speck of dust getting into the apparatus. In spite of every precaution the progress of the work was hampered a great deal owing to this cause.

Of other possible methods of measuring surface tension, that of the sessile drop seemed to meet the requirements most satisfactorily. It has recently been employed by Richards and Boyer (*Journ. Amer. Chem. Soc.* xliii. p. 274, 1921) for both mercury and liquid gallium, but was in use as far back as the time of Laplace. Quincke (*Ann. Physik*, cv. p. 38, 1858) was the first to make the most extensive use of the method, not only for mercury, but for a variety of other liquids, and seems to have made the first attempts to measure accurately the distance from the top of the drop to its maximum diameter. In the case of large drops this distance, h , is connected with the surface tension by the relation

$$h^2 = a^2 = \frac{2\sigma}{\rho g},$$

ρ being the density of the liquid.

The most complete study of the forms of sessile drops of mercury is that of Bashforth and Adams ('An Attempt to test the Theories of Capillary Action': Cambridge University Press, 1883). Their method is to trace out successive small portions of the curve of the drop by means of the differential equation to the curve, "the increments of the coordinates being developed in series proceeding according to ascending powers of the increment of the quantity chosen as independent variable." The procedure is very long and tedious, but its accuracy is unquestioned. The most interesting result of their investigation is the relationship of the capillary constant a , the distance h , and the radius (maximum) of the drop.

From measurements made on their published diagrams and on reference to their tables, it is found that h gradually approaches the value of a (see Table I.) as the drop increases in radius from 1.9 mm. to 4 mm.

TABLE I.

Relationship of h and a for Drops of different Radii.
(Bashforth and Adams's tables.)

Radius of Drop.	h .	$\sqrt{\frac{2}{a}}$	$\sqrt{\frac{1}{a}} = a$.
1.905 mm.	1.499 mm.		
2.515 "	1.854 "		
2.972 "	2.034 "		
3.353 "	2.134 "		
3.658 "	2.209 "		
3.990 "	2.235 "	3.167 mm.	2.241 mm.

It would not be satisfactory to employ drops less than 1 cm. in diameter, and in most of the experiments described in this paper the diameter was usually 1.5 cm. It is to be remarked, however, that the value of a computed from Bashforth and Adams's tables is exceptionally low—2.241 mm. Most experimenters have found values for a varying from 2.5 to 2.8 mm., and it is to be expected that these differences are due to varying degrees of contamination of the mercury surface.

Ferguson (Phil. Mag. xxv. p. 507, 1913) has deduced a relationship between h and a which is very similar to an equation originally given by Poisson (*Nouvelle Théorie de*

l'action capillaire,' p. 212), and involves a first-order correction of considerable magnitude. I do not know what to make of this equation, as it yields results nearly 25 per cent. lower than those calculated from the simple equation

$$h^2 = \frac{2\sigma}{\rho g}$$

for drops 1.5 cm. in diameter ; and these latter calculations are more nearly in agreement with the surface-tension values by the drop method. Now, the drop method has been shown to rest on at least an *experimentally* sound basis, and is hardly likely to give rise to an error as great as 25 per cent. In all the experiments described in this paper I have computed the surface tension with the aid of the simplified equation given above ; and as the diameter of these sessile drops was 1.2–1.5 cm., some idea of the order of magnitude of the correction term can readily be formed by those who consider the correction necessary.

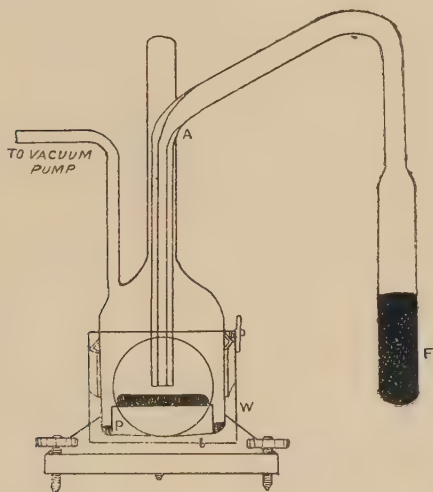
The use of very large drops is unnecessarily cumbersome, especially as the measured height h is found to have a constant value after a certain diameter is reached.

Most experimenters form a globule of mercury on a horizontal surface with the aid of a pipette, which is no doubt very thoroughly cleaned, but probably results in some inevitable contamination of the mercury surface. I have adopted a more satisfactory method of distilling over a quantity of mercury *in vacuo* on to a clean glass plate, a very small depression being made in the centre of the plate to assist the formation of the first portions of the globule. The procedure will be readily understood from fig. 1, and its success depends on the form of the curvature of the capillary tube at A. If the distillation is carried out properly and the glass surfaces are absolutely clean, the small globules of mercury should roll over the surface and pass down the capillary without clogging at A. The chances of surface contamination are minimized in this way, but too great emphasis cannot be laid on the necessity for rigorous cleaning of all portions of the glass that are likely to come into contact with the mercury. The apparatus should be treated with hot chromic acid, with nitric acid and alcohol, and also, if necessary, with pure boiling alcohol for some time. This applies more especially to the glass plate on which the mercury globule rests. Such treatment, however, may not always remove all the impurities adhering to the

surface. Gas films and water films may have to be removed by outgassing the apparatus at high temperatures, but there are reasons now for believing that such films are only of secondary importance so far as contamination of the surface is concerned.

Observations of the drop were made with a cathetometer through the window W of plane, optical glass cemented on to a circular opening in the main chamber of the apparatus. No satisfactory cement made of inorganic materials was found which could be used with high vacua. A variety of

Fig. 1.



red sealing-wax worked fairly well ; it should be put on at a temperature of 110°C . The wax should not be heated too much, otherwise vapours will be given off which will foul the interior of the chamber. If necessary, the interior must be re-cleaned, with the window cemented in position. The experimental conditions would be very much improved if such adhesives could be done away with. After some time impurities from the wax undoubtedly creep over the surface of the glass, and the apparatus has to be taken to pieces and re-cleaned from time to time.

An accurate cathetometer made by the Cambridge and

Paul Instrument Co. was used to measure the dimensions of the drop, the outline of which was brought into focus by the telescope of the cathetometer against a strongly illuminated background. In locating the maximum diameter of the drop, I have adopted the method of Richards and Boyer (*loc. cit.*). A small filament lamp was lit some distance behind the telescope and on the same level with it. The lamp was reflected from a point on the maximum diameter as a tiny spot of light, which could be brought to a focus and located with fair accuracy by the cross-hairs of the telescope. The distance h in mm. from the top of the drop to the maximum diameter is given in the tables to one in the third place of decimals, as it is usually the average of a number of readings; but the order of accuracy is probably about ± 0.0005 mm. Richards and Boyer (*loc. cit.*) quote some of their results to one in the fourth place, and attribute the great variation in the value of h for different drops of mercury to the difficulty of adjusting optical conditions to perfect uniformity. I am inclined to think that the variations are too great to be due to this cause alone, and it is more likely that they are the result of variable contamination of the surface.

*Reversible and Irreversible Adsorption at a
Mercury Surface.*

In carrying out the determinations with the apparatus described, the whole system is evacuated for some hours to a pressure of 10^{-5} mm. or less with the aid of a mercury-vapour pump. The mercury is then carefully distilled from the flask F to form a globule of the necessary dimensions on the plate P. It very often, though not invariably, happens that the surface tension of the first globule formed is very low, but it continues to rise as successive quantities of mercury are distilled over to form new globules. It appears as though the first portions of mercury removed some impurity from the glass surface; but sometimes the tension tends to fall slightly again on distilling further quantities of mercury. Some results of a typical experiment of this kind are given in Table II.

TABLE II.

Temperature 19°·5 C.

Successive drops No.	<i>h.</i> (mm.)	Surface tension. (dynes per cm.)
1	2·545	430
2	2·584	444
3	2·570	439
4	2·580	442
5	2·618	455
6	2·610	453
7	2·625	458
8	2·634	461
9	2·665	472
10	2·634	461
11	2·645	465
After remaining for twenty-four hours in the vacuum :		
	2·590	446
Dry, purified air admitted at 760 mm. After one hour :		
	2·588	445
More mercury distilled at 10 ⁻⁵ mm., after re-cleaning apparatus :		
1	2·580	442
2	2·587	445
Unpurified air from laboratory admitted. After 5 minutes :		
	2·534	427
After one hour :		
	2·485	410
Apparatus re-evacuated to 10 ⁻⁵ mm. :		
	2·490	412

The admission of pure dry air to a mercury surface formed in a vacuum does not appear to alter its tension very much, but the chances of contamination from the ordinary air of the laboratory are very great. The tension falls to a very low value, and does not rise again on re-evacuation of the system. The contamination in this case is completely irreversible. The effect of raising the surface tension by shaking or vibrating the drop, a phenomenon noted especially by Quincke, is only of a temporary nature, and the drop settles down to its original condition in a very short time. The vibration may temporarily disturb the orientation of the

molecules of the adsorbed impurities, but it is evident that they cannot be made to leave the surface, even under very high vacua.

In extreme cases the tension has fallen by irreversible contamination to as low a value as 296 dynes per cm. ($h=2.110$ mm.). I have frequently observed that whenever it is found impossible by reason of the dirtiness of the apparatus to form drops with high surface tensions, the surfaces very quickly become contaminated, with a progressive fall in the tension.

These results are in harmony with those obtained by the drop method. When a surface is formed in air at atmospheric pressure, the presence of the air may hinder the adsorption of the impurities, but the admission of air to a surface already formed in a vacuum does not appear to result in a desorption of the impurities. In fact, it seems to have a slight lowering effect on the tension, and sometimes, if not purified, it may reduce it to a much lower value than was possible in the vacuum under the given conditions.

The view has been held that liquid mercury is composed of different sorts of complex molecules, and that changes in its surface tension with time are due to the slow accumulation at the surface of those modifications possessing the lower tension (see Bancroft, 'Applied Colloid Chemistry,' p. 134, 1921). The experiments described in this paper do not substantiate this argument. Moreover, we have evidence from another source (Smits, *Zeitsch. Physik. Chem.* lxxvii. p. 378, 1911) that mercury behaves as a unary substance.

It is impossible to believe that the contamination of the surface is due to water vapour adsorbed from the glass as originally suggested. I have taken a globule of mercury with a clean surface (tension about 470 dynes per cm.), and exposed it to water vapour up to the saturation pressure (temperature $20^{\circ}5$ C., pressure 18 mm.). The results were not very interesting, as the effect of water vapour on the tension is rather small :

Pressure of water vapour. (mm. Hg.)	h . (mm.)	Surface tension. (dynes per cm.)
13.5	2.610	453
18.0	2.597	449

These figures, however, are in fairly good agreement with those obtained by the drop method (*Phil. Mag.* xlviii. p. 180, 1924), using an air-water vapour mixture. But it has not

been found possible to condense the water on to the mercury surface at the saturation pressure. By slightly warming the bulb containing the water with the hand, the water readily condenses on the walls of the apparatus, but there is no change in the tension of the mercury. In the drop-weight experiments, the mercury surface was formed very near to the water surface, and in this vicinity momentary conditions of super-saturation might prevail, favourable to the rapid condensation of the water. The theoretical aspects of this phenomenon, however, are discussed in a later part of this paper.

Further adsorption experiments have been carried out with the vapours of certain organic liquids, no admixture with air being allowed in these cases. The liquids were contained in small bulbs communicating with the apparatus and kept at various temperatures to give vapours of different pressures. The apparatus was first of all exhausted to a pressure below 10^{-5} mm., a satisfactory globule of mercury formed by distillation, and after shutting off this part of the system from the pumps the vapour of the organic liquid was allowed to enter the chamber containing the globule. The pressure of the vapour was recorded by a mercury manometer, and could be varied within certain limits by shutting off the vapour from the liquid supply and expanding it into the main part of the system. The reversibility of the adsorption could be tested by this means, as changes in the shape of the globule could be observed as the vapour pressure was first increased and afterwards reduced to its original value. As the temperature coefficient of the surface tension of mercury is not very large, it sufficed for the present purpose to work in a room of fairly constant temperature.

Table III. records some results with the vapour of benzene, which indicate that the adsorption is a partly reversible phenomenon. But it seems practically impossible to remove the last traces of vapour from the surface. These data are expressed graphically in fig. 2, and the points marked with squares are those which were obtained by reducing the pressure to its original value after reaching the saturation point. They mark the limits of reversibility of the process.

The results are in fair agreement with those previously obtained by the drop method, using air-vapour mixtures, and, as will be shown later, give much the same value for

the area per molecule of adsorbed benzene on the mercury surface.

Fig. 2.

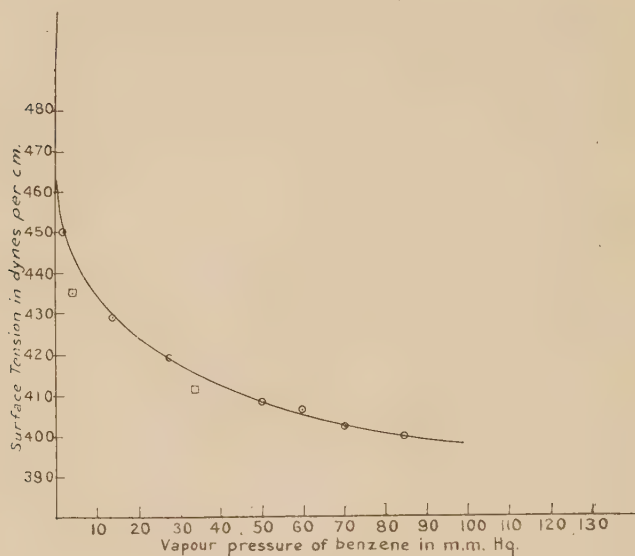


TABLE III.

Surface-tension Changes in Benzene Vapour.
Temperature 23° C.

Pressure. (mm. Hg.)	<i>h</i> , (mm.)	Surface tension, (dynes per cm.)
2.0	2.600	450
14.0	2.540	429
27.5	2.512	419
50.5	2.479	408
60.0	2.473	406
70.0	2.458	402
84.5	2.450	399
Brought back to :		
33.5	2.488	411
4.0	2.560	435
10 ⁻⁵	2.558	434

I have obtained some remarkable results with a sample of

benzene of doubtful purity which are recorded in Table IV. The adsorption in this case appears to be completely irreversible; but it is difficult to put any interpretation on these results, as we do not know how much this effect may be due to traces of sulphur compounds in the benzene.

TABLE IV.

Irreversible Changes of the Tension in Benzene Vapour.
Temperature 21° C.

Pressure. (mm. Hg.)	h , (mm.)	Surface tension. (dynes per cm.)
33.0	2.473	406
51.0	2.352	368
73.5	2.227	330
Brought back to:		
1.0	2.228	330
After 20 minutes:	2.145	306
On re-evacuating to 10^{-3} mm. and continual shaking of drop, h rose to 2.510, and rapidly fell again to 2.177.		

I have not followed up this phenomenon any further at present, but have observed that sometimes an irreversible contamination may take place concurrently with the adsorption of the vapour, and that this contamination is not necessarily derived from the vapour. It is safer to start with a clean surface of mercury and observe it for some time before admitting the vapour, so as to be certain that it is not being progressively contaminated in the vacuum itself.

The results of experiments with ethyl alcohol are recorded in Table V. and fig. 3, and with propyl chloride and ethyl

TABLE V.

Surface-tension Changes in Ethyl Alcohol Vapour.
Temperature 21° C.

Pressure. (mm. Hg.)	h , (mm.)	Surface tension. (dynes per cm.)
1.0	2.605	451
8.5	2.570	439
12.0	2.555	434
17.0	2.540	429
26.5	2.522	423
47.0	2.498	415
Brought back to:		
2.0	2.570	439

Fig. 3.

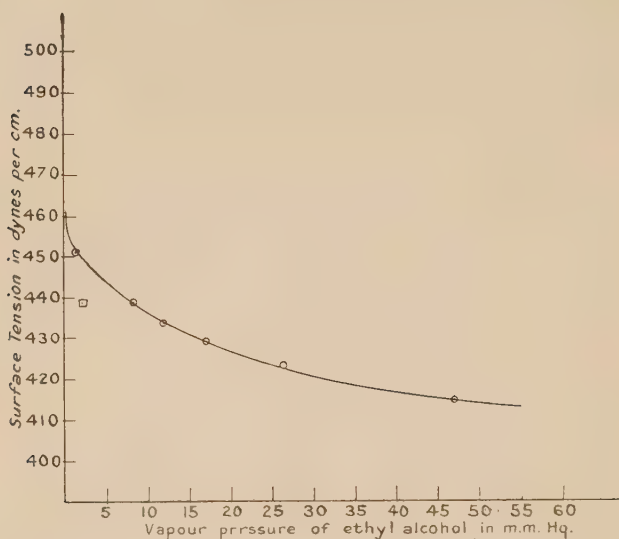
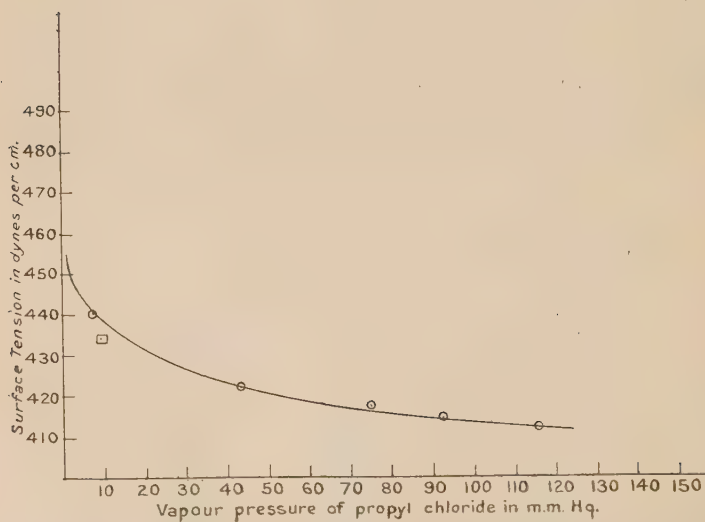


Fig. 4.



bromide in Tables VI. and VII. and figs. 4 and 5 respectively. As in the case of benzene, the adsorption of these

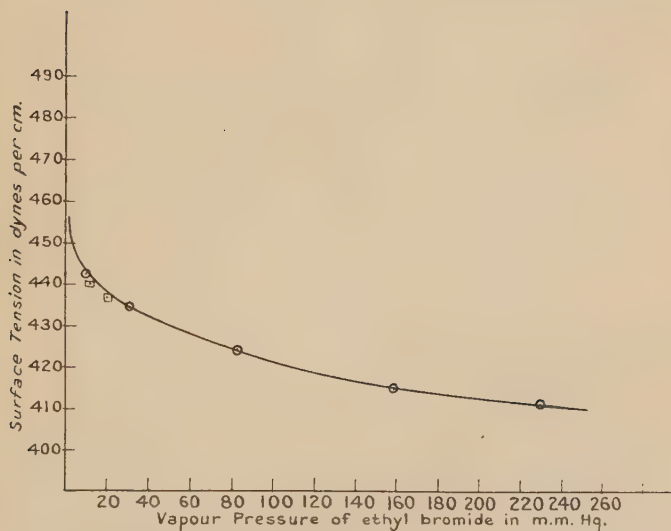
substances appears to be within certain limits a reversible phenomenon. It is remarkable that these substances, which are more definitely polar than benzene and, especially in the

TABLE VI.

Surface-tension Changes in Propyl Chloride Vapour.
Temperature 21° C.

Pressure. (mm. Hg.)	<i>h</i> . (mm.)	Surface tension. (dynes per cm.)
7.0	2.575	440
43.5	2.519	422
75.0	2.505	417
93.0	2.492	413
116.0	2.485	411
Brought back to :		
9.0	2.555	434

Fig. 5.



case of the alkyl halides, possess an atom or group more likely to form a definite linking at the mercury surface, should have no more marked effect on the surface tension than benzene itself.

TABLE VII.

Surface-tension Changes in Ethyl Bromide Vapour.
Temperature 22° C.

Pressure. (mm. Hg.)	<i>h</i> . (mm.)	Surface tension. (dynes per cm.)
10.0	2.580	442
31.5	2.559	434
82.5	2.527	424
158.0	2.495	414
230.0	2.480	411
Brought back to :		
20.0	2.565	437
11.0	2.575	440

In the case of methyl iodide, however (Table VIII. and fig. 6), a very decided change in the nature of the adsorption was observed. Not only was the tension lowered to a much greater extent, but the adsorption appeared to be completely irreversible.

TABLE VIII.

Surface-tension Changes in Methyl Iodide Vapour.
Temperature 22° C.

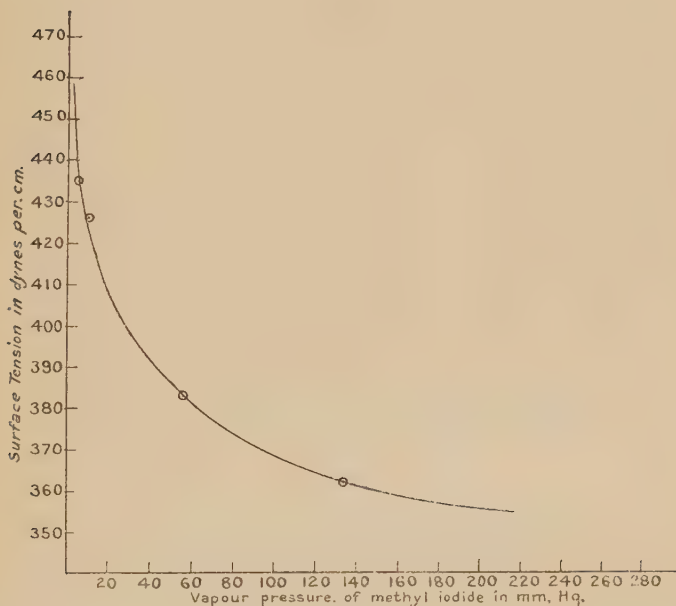
Pressure. (mm. Hg.)	<i>h</i> . (mm.)	Surface tension. (dynes per cm.)
4.5	2.560	435
10.5	2.531	426
56.0	2.400	383
134.0	2.335	362
Brought back to :		
7.0	2.335	362

(No increase in the tension on re-evacuation to 10^{-5} mm.)

Now mercury is known to form—at least in sunlight—a definite chemical compound with methyl iodide (Frankland, *Annalen*, lxxxv. p. 361, 1853; Whitmore, ‘Organic Compounds of Mercury,’ p. 89, 1921), and it is possible that the molecules of this substance are held at the mercury surface with a much greater tenacity than in the case of the other halides. This might be regarded as a low temperature analogue of an interesting phenomenon occurring at high

temperatures—the irreversible adsorption of oxygen by tungsten studied by Langmuir (Journ. Amer. Chem. Soc. xxxv. p. 105, 1913; *ibid.* xxxviii. p. 2272, 1916). The oxygen atoms, however, are not regarded as forming a definite oxide at the tungsten surface, but rather some form of stable adsorbed film, in which the valency bonds of the oxygen atoms are fully saturated; but the valencies of the tungsten atoms on the surface are still partially saturated by union with the atoms in the layer beneath. It might be possible

Fig. 6.



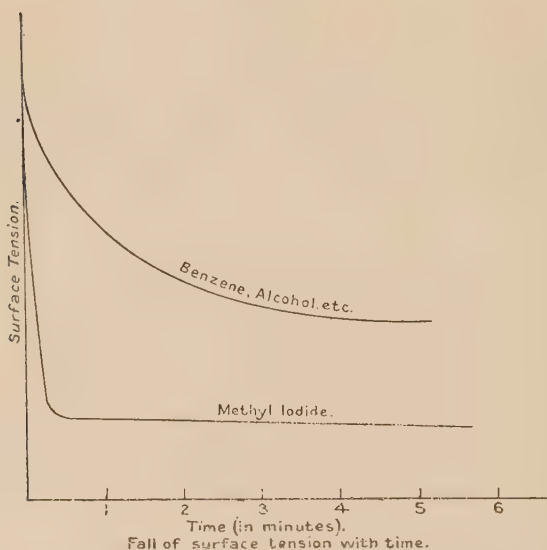
to apply a similar reasoning to the methyl iodide case, and this will be discussed presently in dealing with the space taken up by the molecules on the mercury surface.

A definite surface compound would be quite a different thing from the average adsorption film held at the surface by secondary valence forces, which may be likened to a kind of surface solution. In the above case, the methyl-mercuric iodide may have a definite dissociation pressure of its own; but it must be noted that we reach the adsorption

maximum along a curve very similar to that of any of the other substances which show reversible adsorption.

This brings up the interesting question of the rate of adsorption, as it might be thought that at low pressure the process was a very slow one, and that equilibrium was not always reached under the given experimental conditions. I have given some curves (fig. 7) to show how quickly the surface tension falls with time; but this is only an approximation, as it is a very difficult matter to measure the tension when it is changing so rapidly, owing to the impossibility of

Fig. 7.



making the necessary optical adjustments within the short space of time required. I have observed, however, that for moderately high vapour pressures, 40–50 mm., the adsorption of the methyl iodide is much more rapid than that of any of the other substances examined. The rate of desorption in the reversible process seems to be quite as rapid as the adsorption itself; but this part of the technique of the method will have to be improved considerably before any reliable results can be expected.

It has been said that the tension may sometimes continue

to change with time quite independently of the vapour. I have often observed, however, that after the mercury surface has been in contact with the vapour for an hour or more, the tension was very little different from what it was at the end of the first five minutes. It may safely be said that the adsorption equilibrium is reached in every case within a few minutes.

Purity of Materials.

The benzene was Kahlbaum's "Thiophen frei," and was redistilled after standing over phosphoric oxide.

The ethyl alcohol was practically anhydrous. It gave a negative test with a crystal of potassium permanganate, and was free from aldehydes as indicated by the silver nitrate test. The presence of traces of other homologues was not thought likely to be objectionable in the present experiments.

The methyl iodide was purified by shaking with dilute alkali, drying over calcium chloride, and distilling, the major portion boiling at $42^{\circ}.5$ C. (760 mm.) being collected. It was redistilled from silver-foil, and kept over a small quantity of silver in an amber-coloured bottle. The bulb of the apparatus containing the methyl iodide was shielded from the light during the experiments.

The ethyl bromide and propyl chloride were Kahlbaum's pure chemicals, and were used immediately after opening the sealed bottles.

Methods of Calculating the Adsorption.

In the previous paper of this series (Phil. Mag. xlviii. p. 187, 1924) reference was made to the difficulty of calculating the amount of the saturated adsorption owing to the form of the σ - p curve. It so happens in most of these instances that the surface tension is some logarithmic function of the pressure, so that the value of $\frac{d\sigma}{dp}$ does not always afford a convenient means of calculating the adsorption coefficient Γ .

It is possible to express these relationships in the form of an equation very similar to Szyskowski's (*Zeitsch. Physik. Chem.* lxiv. p. 385, 1908), which Langmuir has made use of

(Journ. Amer. Chem. Soc. xxxix. p. 1885, 1917) to calculate the adsorption coefficient in a number of instances. I have thought it worth while to re-calculate the values for the saturated adsorption of benzene and methyl acetate with the aid of this derived form of Szyskowski's equation, and to compare them with the previous values obtained by the use of the tangent to the σ - p curve.

Inserting vapour pressure for concentration in the original Szyskowski equation, we have :

$$\frac{\sigma}{\sigma_0} = 1 - B \log \left(\frac{p}{A} + 1 \right),$$

where σ_0 = surface tension of mercury,

σ = surface tension for any particular vapour pressure p ...,

B & A are constants.

Langmuir (*loc. cit.*) has shown that, by differentiating this equation and comparing it with the Gibbs adsorption equation, the limiting amount of adsorbed vapour will be expressed by :

$$\Gamma = \frac{0.434 B \sigma_0}{RT}$$

in gram molecules per square centimetre.

Now, in finding the value of the constant B , I have adopted the original method of Szyskowski. To values of $\frac{\sigma}{\sigma_0}$ differing by constant increments, I have found corresponding values of σ and p from the smoothed σ - p curve ; Δp are the successive increments of p , and $\frac{\Delta p_{n+1}}{\Delta p_n}$ their ratios (R). If the logarithmic law be followed, R should be a constant ; and it appears to be so within the limits of accuracy of Szyskowski's own data on which Langmuir bases his general conclusions. Now, if n be the number of successive increments of $\frac{\sigma}{\sigma_0}$, and d the value of this increment,

$$B = \frac{nd}{n \log R} = \frac{d}{\log R}.$$

TABLE VIII. (a).

$\frac{\sigma}{\sigma_0}$	σ	p	Δp	$\frac{\Delta p_{n+1}}{\Delta p^n}$
0.840	396.5	72.0	17.0	
0.850	401.2	55.0	12.2	(1.40)
0.860	405.9	42.8	9.1	1.34
0.870	410.6	33.7	7.5	1.22
0.880	415.4	26.2	6.0	1.25
0.890	420.1	20.2	4.5	1.33
0.900	424.7	15.7	3.4	1.32
0.910	429.4	12.3	2.6	1.30
0.920	434.2	9.7	2.1	1.24
0.930	438.9	7.6	1.7	1.24
0.940	443.6	5.9		
			Mean (R)	 1.28

Hence

$$B = \frac{0.01}{\log 1.28} = \frac{0.01}{0.1092} = 0.0961,$$

so that

$$\begin{aligned}\Gamma &= \frac{0.434 \times 0.0961 \times 472}{8.4 \times 10^7 \times 299} \\ &= 0.078 \times 10^{-8} \text{ gram molecule per sq. cm.} \\ &= 0.0473 \times 10^{16} \text{ molecules per sq. cm.}\end{aligned}$$

$$\therefore \text{area per molecule} = 21.2 \times 10^{-16} \text{ sq. cm. ;}$$

$$\text{previously found value} = 21.0 \times 10^{-16} \text{ sq. cm.}$$

From the data obtained with methyl acetate it is found in a similar way that

$$B = 0.0715,$$

$$\begin{aligned}\Gamma &= 0.0583 \times 10^{-8} \text{ gram molecule per sq. cm.} \\ &= 0.035 \times 10^{16} \text{ molecules per sq. cm.}\end{aligned}$$

$$\therefore \text{area per molecule} = 28 \times 10^{-16} \text{ sq. cm. ;}$$

$$\text{previously found value} = 27 \times 10^{-16} \text{ sq. cm.}$$

The agreement between the values calculated by the two methods may be considered as satisfactory.

The adsorption coefficient has also been calculated from the data on the lowering of the surface tension of the sessile

drop. The results obtained by this method are not likely to be of the same order of accuracy as those computed by the drop method; but in the case of benzene the agreement is fairly satisfactory.

Γ was found to be 0.0726×10^{-8} gram molecule per sq. cm., giving an area per molecule on the surface of 23×10^{-16} sq. cm., which is a little larger than the previously found value.

For ethyl alcohol, $\Gamma = 0.0567 \times 10^{-8}$ gram molecule per sq. cm., and the area per molecule, 29×10^{-16} sq. cm. It is interesting to compare this with the value found for the area (29×10^{-16} sq. cm.) from the data of Bircumshaw (Journ. Chem. Soc. cxxi. p. 887, 1922) on the surface tension of water-ethyl alcohol mixtures. The agreement is striking, but it is doubtful if the results are strictly comparable. In the case of substances adsorbed on the surface of water, it is usual to imagine some form of solubility such as affects the polar group of the molecule. With the mercury surface this assumption would not be feasible. We must imagine some kind of linking of the atoms at the surface, whereby the area per molecule of adsorbed substance is determined partly by the specific group attached to the surface, but more especially by the spacing of the mercury atoms themselves. In connexion with this there are some crystallographic data (McKeehan and Cioffi, Phys. Rev. xix. p. 444, 1922; Debierne, *Comptes Rendus*, clxxiii. p. 140, 1921) from X-ray examination of both solid and liquid mercury, but they are not considered satisfactory (Wyckoff, 'Structure of Crystals,' p. 243, 1924). It is noteworthy, however, that the molecule of methyl iodide appears to occupy only about half or a third the space appropriated by the molecules of the other substances (Table IX.). Now it is fairly certain

TABLE IX.

	Area per molecule in sq. cm. $\times 10^{16}$.
Methyl acetate	27.5
Benzene	21-23
Ethyl alcohol	29
Propyl chloride	ab. 40
Ethyl bromide	ab. 40
Methyl iodide	13

that the formula of methyl-mercuric iodide is $\text{CH}_3\text{—Hg—I}$. If we imagine that this compound is actually formed at the mercury surface, and that with the saturated adsorption all the available spaces of the surface are covered, then every

mercury atom will be united by two bonds to the methyl group and the iodine atom respectively. But such an arrangement might not satisfy at the same time our idea of the electronic configuration of the system, and it would be better, from the analogy of the oxygen atoms on the tungsten surface, to imagine the methyl group and the iodine atom as each attached to a separate mercury atom, which is itself partially saturated by union with a mercury atom in the layer beneath. The area for each mercury atom on the surface will then be 6.5×10^{-16} sq. cm. It is evident that the molecules of the other substances are not packed so closely at the surface, nor are they held there with such tenacity; but it is not proposed to discuss this matter any further until more extensive data, particularly on the heats of adsorption, are obtained.

General Theory of Adsorption and Condensation.

It has been necessary in all these cases to postulate in the first instance the existence of a monomolecular film, and afterwards to calculate on this assumption the space appropriated by each molecule on the surface. But we might also suppose that only a small part of the surface is covered with the adsorbed molecules, and that there is a gradual decrease in the density of the vapour outwards from the surface through a layer several molecules thick. This assumption, however, would not be in accord with the usually accepted idea of the nature of molecular attractive forces, and certainly not in agreement with the very convincing theories of Langmuir and Harkins, based as they are on some very conclusive experimental evidence.

Now, the film of discontinuity imagined by Gibbs was an essentially different thing. In his day, and until quite recently, it was usual to regard such a film as forming, what Hardy termed, a composite surface. The tension of such a film formed from the saturated vapour would be written $\sigma_A + \sigma_{AB}$, where σ_{AB} is the interfacial tension of the film and the liquid beneath it, and σ_A the surface tension of the liquid composing the film, assuming also that the two liquids are mutually insoluble. The condition of the film as it thinned to molecular dimensions was largely a matter of speculation. Hardy's interesting experiments on the tension of composite surfaces (Proc. Roy. Soc. lxxxviii. p. 312, 1913), especially with reference to the spreading of certain liquids on water, did not reveal the essential difference between the film formed from the vapour and the thicker film formed by the spreading liquid. But it was obvious that certain substances

would form very thin films by adsorption of the vapour by the water that normally would not spread on water. The tension of such thin films could not be $\sigma_A + \sigma_{AB}$, as this was greater than the surface tension of water, σ_B .

Now, Gibbs imagined ('Scientific Papers,' i. p. 235) that the saturated vapour of water would form a thick film on a mercury surface whose tension was equal to $\sigma_A + \sigma_{AB}$. He quoted some figures of Quincke, and indicated that if we knew the surface tension of mercury under different pressures of water vapour up to the saturation value, we could calculate the amount of water on the surface, and hence find the thickness of the film. Quincke's figure for the tension of mercury at 20° C. is 539 dynes per cm., and for $\sigma_A + \sigma_{AB}$ 81+417=498 dynes per cm. If experiments had been carried out to determine the surface tension of mercury for intermediate pressures of water vapour, a nearly linear relationship between the pressure and the tension would have been found. The pressure and density of water vapour at 20° C. are 17.5 mm. Hg. and 0.0000174 gram per c.c. respectively. Hence

$$\Gamma = 0.0000174 \times \frac{41}{1.75 \times 981 \times 13.6} = 3 \times 10^{-8} \text{ gram per sq. cm.}$$

the exact requirement for a monomolecular film.

Since the film was imagined to possess the properties of liquid water in mass, being in equilibrium with the saturated vapour, such a result would have been regarded as an anomaly, as it was in conflict with the theory of molecular dimensions; and the concept of a monomolecular film having the tension equal to $\sigma_A + \sigma_{AB}$ is something entirely novel, and would not have been considered as adequately representing the facts.

But in how many cases, it may be asked, other than water,

TABLE X.

	σ_A .	σ_{AB} .	$\sigma_A + \sigma_{AB}$.	σ_m .
Water	73	375	448	449
Methyl acetate.....	25	370	395	412
Benzene	28	354	382	395
Ethyl alcohol	22	364	386	415
Methyl iodide	35	304	339	349

(Some of these figures are taken from the data of Harkins and Grafton (Journ. Amer. Chem. Soc. xlii. p. 2543, 1920) on interfacial tensions.)

is this relation true? I have given in Table X. some figures for σ_m , the tension of the monomolecular film in the saturated vapour, and for $\sigma_A + \sigma_{AB}$, and it will be seen that σ_m is usually somewhat greater than $\sigma_A + \sigma_{AB}$.

Now it has been shown very conclusively by Gibbs ('Scientific Papers,' i. p. 258) that the most stable film between two phases such as these, the vapour phase of the substance A and the liquid phase B, would have the tension $\sigma_A + \sigma_{AB}$, provided that $\sigma_A + \sigma_{AB} < \sigma_B$, which is certainly the case for these films on the mercury surface. Gibbs, however, did not consider the possibility of building up a film from successive layers of molecules, and unless we knew how the tension changed with each layer, we could not find out how σ_m approached the value $\sigma_A + \sigma_{AB}$; for in all real changes the diminution in free surface energy per gram molecule of adsorbed substance cannot be less than the external work required to condense the gram molecule from the vapour state.

But there are some special instances where it seems fairly certain that $\sigma_m = \sigma_A + \sigma_{AB}$. I refer to the interfacial tension of two liquids slightly soluble in one another. The relationship is known as Antonoff's law (Antonoff, *Journ. de Chim. Phys.* v. p. 372, 1907; Hardy, *Proc. Roy. Soc. A*, lxxxviii. p. 313, 1913), and expresses the fact that this interfacial tension is equal to the difference of the tensions of the two liquid phases. Reynolds (*Trans. Chem. Soc.* cix. p. 466, 1921) has adduced some experimental evidence in support of this law. Now, in the case of benzene and water, the tension of water saturated with benzene is the same as the tension in the saturated vapour of benzene, and is equal to σ_m . The tension of the benzene saturated with the water is very little greater than the tension of benzene itself, σ_A . According to Antonoff's law, $\sigma_m - \sigma_A = \sigma_{AB}$ or $\sigma_m = \sigma_A + \sigma_{AB}$. There are not sufficient data to enable one to say if this law is capable of universal application.

There must be some cases, of course, where $\sigma_m < \sigma_A + \sigma_{AB}$; and this is to be found when the vapours of certain saturated organic substances, such as carbon disulphide, lower the surface tension of water; but the substances themselves cannot spread on the water, since $\sigma_A + \sigma_{AB} > \sigma_B$.

With mercury, however, the experimental results have in many cases indicated a very great fall in the tension when the mercury surface is formed in the saturated vapour; and this fall occurs most rapidly when the mercury is near the surface of the other liquid. Owing to the slight temperature fluctuations of the thermostat, momentary conditions of supersaturation of the vapour may occur, favourable to a rapid condensation of the vapour in this vicinity; and it has been argued, with some justification, that the films formed in this way are of unusual thickness compared with the primary

adsorption films. As far as changes in the tension are concerned, what must happen is this: with the primary adsorption of a monomolecular film, the drop registers a tension which is that of a composite surface and may be of the order $\sigma_A + \sigma_{AB}$. As each layer of molecules is added to the film to form a new and independent surface of the condensed liquid, the drop begins no longer to register the tension of the composite surface, but rather the interfacial tension σ_{AB} . But what concerns us most is the change, if any, in the orientation of the first layer of molecules adjacent to the mercury surface. It is impossible not to believe that some change has taken place, because the tension associated with this first layer has fallen from $\sigma_A + \sigma_{AB}$ to σ_{AB} . It seems reasonable, therefore, to assume that the molecules become more closely packed at the surface during the condensation process; but, if so, this change in the orientation must be due to an intermolecular attraction extending through a layer many molecules thick.

But as long as σ_m is of the order $\sigma_A + \sigma_{AB}$, condensation under isothermal conditions is thermodynamically impossible; and we must assume, as we have already done, that there is some slight degree of supersaturation of the vapour, in order that the condensation may take place. But a thick film already formed in this way and possessing the tension $\sigma_A + \sigma_{AB}$ would not be unstable under isothermal conditions unless $\sigma_A + \sigma_{AB} > \sigma_m$, in which case it would first break up into lenses and afterwards form the primary film of the tension σ_m . The difficulty of experimentation in these cases would lie in the accurate control of the temperature.

Now, the *interfacial* tension has been used in recent years as the basis of certain calculations of the attraction of one liquid surface for another. It occurs, for instance, in Dupré's equation, $W = \sigma_A + \sigma_B - \sigma_{AB}$, where W is a measure of the attractive forces, the adhesional work; and this has been used by Harkins (Journ. Amer. Chem. Soc. xxxix. p. 354, 1917) in the development of his theory of the orientation of molecules at liquid-liquid interfaces. But Harkins's deductions would lead us to believe that the *interfacial* tension of two liquids is the result of certain molecular rearrangements confined exclusively to the first layer of molecules. This can hardly be the case, as we have seen, that the *interfacial* tension may result from an intermolecular attraction extending through a layer several, or many, molecules thick. His argument, at first sight, seems very convincing, but it is doubtful if his results can be interpreted in so simple a manner.

It is hoped shortly to be able to communicate some results of the direct measurement of the adsorption.

Summary.

It has been shown by two independent methods of measuring the surface tension of mercury, when the mercury surface is exposed to vapours of different pressures, that these vapours adsorb on the surface to give films that, in all probability, are only one molecule in thickness; and the space taken up by these molecules on the surface has been found to agree fairly satisfactorily with data of a similar kind from other sources.

In the saturated vapour, under special conditions, it has been found possible to form films which are of much greater thickness; but it has been argued on thermodynamical grounds that such condensation is impossible under strictly isothermal conditions, if the tension of these films is not less than the tension of the monomolecular films.

The mercury surface has been found to be very easily contaminated by traces of impurities, the source of which has often been difficult to ascertain; but it is possible that they are derived in part from the glass surfaces with which the mercury comes in contact, and are not readily removed by the usual cleaning agents. Such contamination is irreversible, and the adsorbed impurities cannot be removed at ordinary temperatures, even in the highest vacua.

The adsorption of the vapours of certain organic substances has been found to be largely reversible, except in the case of such a substance as methyl iodide, which is known to form a definite compound with mercury. It is considered that the bond of union between the mercury atoms and the halide molecules is of a more pronounced type than in the case of the molecules of other substances. It is suggested that a distinction may have to be drawn between a "surface compound" and a "surface solution," even in these simple cases.

The investigation of the adsorption of vapours on liquid surfaces is considered to open up a new and promising field for the study of adsorption films and molecular structure.

I am indebted to Professor Donnan for the great interest he has taken in this investigation, and to the Department of Scientific and Industrial Research for a grant of money which has enabled me to carry it out.

The William Ramsay Laboratories of
Inorganic and Physical Chemistry,
University College, London,
December 20, 1924.

LXVI. *Notices respecting New Books.*

The History of One Hundred Years of Life of the Leeds Philosophical and Literary Society. By Lieut.-Col. E. KITSON CLARK, 1924. (Jowett & Sowry Ltd., Leeds.)

THIS very interesting and delightful volume chronicles the activities of one of the leading philosophical societies in the country. The Leeds Philosophical and Literary Society was founded in 1818, and has from that time pursued an honourable career. The writer of the volume has chosen the best possible way of commemorating the Centenary in reprinting selections from the actual Reports of the Society year by year. By skilful editing these extracts are made to tell the history of the Society, and indirectly they give a vivid picture of the intellectual interests of the more thoughtful citizens of Leeds during the century which is past.

The initial decision to purchase land and erect a building was made at a general meeting on May 7, 1817, and on July 9 the corner stone of the Court House was laid and a gold sovereign of 1817 and other coins were let in. The first meeting was held in the year 1819 to discuss a paper on "The Effects of Spirituous Liquors on the Human Frame." During the first ten years a great variety of subjects were discussed belonging to Archæology and History (24 meetings), Literature, Art, Pedagogy, and Ethics (54 meetings), Chemistry, Geology, Entomology (56 meetings), Physiology and Biology (18 meetings), Geography, Ethnography (11 meetings), and Economics (11 meetings). Many of the papers discussed have familiar titles. Thus in 1834 there was a discussion "On the general improvement and prosperity of Leeds as affected by the smoke of the factories." Others are not so familiar. Thus in 1848 the president read a paper on "The Principles of Education—for Professional Men, for Females, and for the Working Classes." It is interesting to notice the lecture on "The Colour of the Sky" by John Dalton, in 1828, and a lecture by Silvanus Thompson on "Waves of Sound and the Photophone," in 1880.

In 1840 it is recorded that "the tea and coffee for lectures were made exigible in the case of those only who arrived later than a quarter past seven, the hour of meeting being seven." The curve of unpunctuality varied correctly in inverse ratio to the severity of the penal regulations.

This is a fascinating volume, and if it stimulates others of the older societies of this type to a similar publication, will serve a purpose interesting not only to the professional scientific man.

La Technique du Vide. By L. DUNoyer. (Pp. 225. Paris, Les Presses Universitaires de France. 1924.)

THIS book provides a useful summary of the varied methods of producing and managing vacua. The subject has become of great importance during the past ten years, owing to its applications in

the research laboratory, and in the technical production of lamps, valves, and X-ray tubes. The construction of mercury diffusion pumps is treated in some detail. Holweck's ingenious modification of the Gaede molecular pump will still be new to many people. The account of the many types of manometers, which have been proposed for the measurement of high vacua, serves to emphasize how unsatisfactory such measurements still remain.

Another section deals with the design of vacuum apparatus, the expulsion of occluded gases, etc. It is unfortunate that more information upon the making of glass to metal joints has not been included here. A short account is given of recent work on the disappearance of gases in the electric discharge.

The Earth, its Origin, History, and Physical Constitution. By HAROLD JEFFREYS, M.A., D.Sc., Fellow and Lecturer of St. John's College, Cambridge. (Cambridge University Press, 1924.)

THIS important volume is based to some extent on a set of lectures delivered by the Author in the University of Cambridge during the years 1920-1923. It is the first book in which any attempt has been made to present a *general* view of the present state of geophysics. It is a matter of great importance that a general survey of this kind should be made, and this work should mark a new era in the subject. Up to the present time the subject of geophysics has suffered very much from the fact that the problems with which it is concerned are of such extremely diverse kinds that it is impossible that any worker should have a specialist's knowledge of even a majority of them. And this state of affairs inevitably results in the independent development of different problems, even when the logical relation of the problems is intimate and important, and the feasibility of projected solutions of one can only be adequately evaluated by reference to the state of development of another, both as regards the data available and as regards the state of theorising with respect to it and the probability values to be attributed to the various theories.

In the present volume the desirability of coordinating the data and theory belonging to different problems is stressed at every possible opportunity; and for this reason the book is important also as an example of scientific method. And the matter of geophysics lends itself very readily to such treatment. For during recent years a remarkable feature of geophysics has been the extent to which different lines of attack have led to mutually consistent results. This is the more noteworthy when we take into consideration the very varied nature of the data on which geophysics as a science depends, and, more important still, the very varied nature of the hypotheses on which it depends. In part, however, these hypotheses are well established, as, for example, the laws of gravitation, heat conduction, radioactive disintegration, elasticity, and fluid friction.

The aim of the author has been to discuss the theories of the

main problems of geophysics, and to exhibit their inter-relations. And throughout he has introduced quantitative and not merely qualitative comparison of theory with fact. A large number of the theories advocated have survived the test of quantitative application to several phenomena, while decent burial—with no necessity for any exhumation—has been given to many old favourites.

Such an object as quantitative testing necessarily entails the use of mathematics, and this will probably not make the book any easier for geologists nor prejudice them in its favour. But, as the author points out, “if geophysics requires mathematics, it is the earth that is responsible, not the geophysicist.” The author has, however, been remarkably successful in making the spirit of his arguments intelligible to the non-mathematical reader, for he has on several occasions segregated the part of the argument which necessarily requires mathematical treatment, either open or veiled, and has given a clear statement of the point at which mathematics needs to be introduced and the point at which its use can be discontinued, and has, at the same time, recorded the mathematics for the sake of those who want them for reference. This treatment is plainly preferable to that of some writers, who endeavour by means of protracted discussion in words, to make intelligible to non-mathematicians arguments, which even the trained mathematician or logician requires to have in symbols.

We may conclude by recording our great admiration for the way in which this book has been constructed. It is the rôle of the scientist to take data of all kinds and build on them inductions and general laws. In geophysics, however, the task is especially difficult in view of the vast problems involved and the paucity of experimental, as opposed to observational data and, indeed, the relative paucity even of observational data in comparison with many sciences. The general principles of scientific method have, however, been applied in this book in a notable manner on material of very great interest, important parts of which are due to the insight and logical acumen of the author.

LXVII. *Intelligence and Miscellaneous Articles.*

THE INTERNATIONAL CRITICAL TABLES.

AT the meeting of the International Union of Pure and Applied Chemistry held in London in 1919, the American delegates submitted a proposal for the international compilation of critically prepared tables of the physical properties of chemical substances and technological materials. The proposal was approved by the Union, and the American National Research Council at Washington has since undertaken the financial and editorial responsibility for the undertaking. A Board of Trustees has undertaken to raise the sum of \$200,000 or such part thereof as may be necessary. The editorial responsibility is invested in a Board of Editors, the

Editor-in-Chief being Dr. E. W. Washburn, formerly Professor of Physical Chemistry at the University of Illinois.

To ensure the international character of the Tables, Corresponding Editors have been appointed in the principal countries of the world. It may be added that the Tables are in no sense a commercial undertaking and the members of the Boards of Trustees and Editors and the Corresponding Editors serve in an honorary capacity.

The work of critically examining the data and of compiling the various tables is being carried out by well-known chemists, physicists, engineers, etc., some three hundred in number, who have been chosen for this purpose in the various countries of the world, largely on the basis of recommendations from the Corresponding Editors and their advisory committees.

These experts are not being expected to assume the responsibility of searching the literature, a task which is being carried out in the main by the editorial staff at Washington, but rather to assemble, to examine critically and to select the best value for each constant indicating at the same time the probable uncertainty.

Each portion of the Tables will be published over the name of the cooperating expert who has assumed responsibility for the selection, reliability and accuracy of the data in question. The size of each assignment has been restricted so that the work may be carried out within a reasonable time and without becoming too great a burden for any individual (or cooperating group of individuals) to bear.

The main language employed in the Tables will be English, but the introduction, table of contents, definitions, general explanatory text, and a very complete index will be in English, French, German, and Italian.

The Tables will contain all available information of value concerning the physical properties and numerical characteristics of (a) pure substances, (b) mixtures of definite composition, (c) the more important classes of industrial materials, (d) many natural materials and products, and (e) selected data for certain bodies or systems, such as the earth and its main physical subdivisions, the solar and stellar systems, and certain biological organisms, including man. Publications of the world in many languages have been combed for data and much unpublished information has been collected. The scope of the tables is so immense and of such an unprecedentedly comprehensive character, that special attention has had to be given to the arrangement so as to enable the Tables to be used with facility and dispatch.

For pure chemical substances the data will be assembled in tables of properties, but a certain amount of latitude and duplication will be permitted in some instances, and tables of materials will be employed where it proves to be more convenient.

In some cases no definite value of a constant can be put down, but only upper and lower limits. In other cases a graph may be the best means of indicating the variation of the particular property in question. Whatever method of presentation is employed it

will be such as best to bring out the main purpose of the Tables, which is to take stock of our present quantitative knowledge of material things and to prepare in convenient form a critical digest of such knowledge.

The importance of securing uniformity in the case of fundamental constants, conversion factors, etc., has not been lost sight of, nor the importance of associating, where possible, with the data for a particular specimen or material, a statement of the exact experimental conditions, life history, etc.

The Tables will be issued in a series of volumes comprising a total of about 2500 pages ($9\frac{1}{2}$ in. $\times$ 7 in.), publication extending over about a year and a half. The progress made has been such that the first volume is now in the Press and may be expected during the early months of 1925.

The published price of the Tables will be from \$60 to \$75 for the set, but the Trustees are reserving the privilege of purchasing from the publishers at the rate of \$35 per set whatever number of sets may be required to fill all advance subscriptions received by the National Research Council of America up to a definite fixed date, probably April 1st or May 1st, 1925, after which date the privilege will lapse, and subsequent sales will be handled exclusively by the publishers at the higher rate. \$35 represents only the cost of printing, but the Trustees and the National Research Council are anxious that all scientific men and women shall be given the opportunity of taking advantage of the lower rate. Accordingly, arrangements are being made so that (1) members of a recognised scientific, technical or engineering society, or (2) Universities, research laboratories, libraries, government departments or the like, will shortly be given preferential facilities for purchasing sets at the lower figure before the expiration of the above-mentioned date. Only one such set may be subscribed for by one individual, but a reasonable number of sets may be purchased by organisations such as the above.

The National Research Council will deal with such applications, but all orders placed in the ordinary way through the Trade will be handled by the Publishers at the higher figure.

The Advisory Committee for the British Empire (excluding British North America) consists of Dr. G. W. C. Kaye (Corresponding Editor), Sir Robert Robertson, F.R.S., Dr. W. Rosenhain, F.R.S., Prof. A. W. Porter, F.R.S., Dr. T. E. Stanton, F.R.S., Mr. J. E. Sears (Jr.), Mr. A. C. G. Egerton, and Mr W. F. Higgins as Secretary. Dr. Rosenhain is also acting as Special Editor for Metals and Alloys. It is requested that any correspondence from the British Isles with reference to the Tables should be addressed to Dr. Kaye, The National Physical Laboratory, Teddington, Middlesex.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]